EO/US
PCT/IB97/01033

PA[illegible]NT COOPERATION TREAT[illegible]

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 26 February 1998 (26.02.98)	
International application No.: PCT/IB97/01033	Applicant's or agent's file reference: dea5521/002/
International filing date: 15 August 1997 (15.08.97)	Priority date: 16 August 1996 (16.08.96)
Applicant: CRAIG, Hugh, P.	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International preliminary Examining Authority on:

   26 January 1998 (26.01.98)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was
   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 338.83.38

for the designated Office (DO/US)

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

SILVERMAN, Warren
Haseltine Lake & Co
Imperial House
15-19 Kingsway
London WC2B 6UD
ROYAUME-UNI

Date of mailing (day/month/year): 01 October 1997 (01.10.97)	
Applicant's or agent's file reference: HL55521/002/	**IMPORTANT NOTIFICATION**
International application No.: PCT/IB97/01033	International filing date (day/month/year): 15 August 1997 (15.08.97)

1. The following indications appeared on record concerning:

[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
CRAIG, Hugh, P. P.O. Box 2621 Oxnard, CA 93032 United States of America	US	US
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	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

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	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[X] the International Searching Authority
[ ] the International Preliminary Examining Authority
[X] the designated Offices concerned
[ ] the elected Offices concerned
[ ] other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Céline Faust Telephone No.: (41-22) 338.83.38

001699052

PA _NT COOPERATION TREAT

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

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International application No. PCT/IB97/01033	International filing date (day/month/year) 15 August 1997 (15.08.97)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address	State of Nationality	State of Residence
	Telephone No.	
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	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

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3. Further observations, if necessary:
Please note appointment of agent SILVERMAN.

4. A copy of this notification has been sent to:

☒ the receiving Office
☒ the International Searching Authority
☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Céline Faust Telephone No.: (41-22) 338.83.38

AP

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United States Patent and Trademark Office

December 11, 1997

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: *60/024,046*
FILING DATE: *August 16, 1996*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

D. SMITH
Certifying Officer

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53 (b)(2).

Docket Number SVT 0001P	SVT 0001P	Type a plus sign (+) inside this box ->	+

INVENTOR(s)/APPLICANT(s)

LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
Craig	Hugh	P.	4220 Harbor Boulevard #302 Oxnard, CA 93035

TITLE OF THE INVENTION (280 characters max)

CONDUCTIVE INK COMPOSITION, AND ENVIRONMENTALLY_SAFE METHOD OF PRINTING AND CURING SAME ON DIELECTRIC SURFACES FOR THE MANUFACTURE OF PRINTED CIRCUIT BOARDS

CORRESPONDENCE ADDRESS

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ENCLOSED APPLICATION PARTS (*check all that apply*)

X	Specification	*Number of Pages*	23	X	Small Entity Statement
X	Drawing(s)	*Number of Sheets*	2	X	Other (specify) Certificat of Express ~~Mailing~~

METHOD OF PAYMENT (*check one*)

X	A check or money order is enclosed to cover the Provisional filing fees	PROVISIONAL FILING FEE AMOUNT ($)	$75.00
	The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[X] No.

[ ] Yes, the name of the U.S. Government agency and the Government contract number are: ______

Respectfully submitted,

SIGNATURE William C. Fuess   Date 08/16/96

TYPED or PRINTED NAME William C. Fuess   REGISTRATION NO. (*if appropriate*) 30,054

[ ] Additional inventors are being named on separately numbered sheets attached hereto

PROVISIONAL APPLICATION FILING ONLY

CONDUCTIVE INK COMPOSITION, AND ENVIRONMENTALLY-SAFE METHOD OF PRINTING AND CURING SAME ON DIELECTRIC SURFACES FOR THE MANUFACTURE OF PRINTED CIRCUIT BOARDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to printed circuits, especially those produced by printing conductive ink onto a dielectric substrate.

The present invention particularly relates to compositions of inks that are conductive by virtue of containing metal(s), and the use of such conductive inks in the manufacture of printed circuit boards.

2. Description of the Prior Art

2.1 Nature and Uses of Printed Circuit Boards

It is well known in the prior art that printed circuit boards are a highly cost effective and space saving innovation when used in electrical devices. Prior to the advent of printed circuit boards, it was necessary to run individual wires between each component used in an electrical device. The advent of printed circuit board technology permitted manufacturers who repeatedly utilized the same complex circuit design in a high volume product to (i) eliminate the individual wiring of each component into the system while (ii) providing an integral mechanical support for the circuitry.

More particularly, a printed circuit board has numerous electrically conductive pathways imprinted on a dielectric substrate, most frequently a fiberglass reinforced phenolic or epoxy. The electrical components may then be attached to the printed circuit board with the conductive patterns on the board forming the electrical connections there-between.

2.2 Original, and Still Predominant, Conventional Approaches to the Production of Printed Circuit Boards by Etching

Heretofore, conventional methods of forming the electrical pathways of a printed circuit board were both expensive and time consuming. For example, in one process, the dielectric substrate is coated over its entire surface with a sheet of conducting metal, such as copper or aluminum. This is generally accomplished utilizing an electroplating technique. The selected pattern or matrix, which will represent the electrical pathways between the components, is then cut into a cloth material such as silk. The cloth material, having the cut-out matrix is then placed on the dielectric substrate which has been previously coated with the conducting material. An etch-resist ink is then rolled over the cloth, with the ink passing through the cut-out pattern and forming an inked matrix on the coated dielectric substrate. The above described method is a conventional silk screen technique. The inked and coated board is then subjected to light which causes the etch-resist ink to become acid resistant. The dielectric substrate is then treated with acid

such that all the metal areas of the board not coated with the ink are etched away leaving just the matrix pattern. The ink itself may then be removed by conventional techniques thereby leaving the electrically conductive pathways formed on the printed circuit board.

In another method used in the prior art, a catalyst is placed on an un-coated dielectric substrate in the desired wiring matrix. The substrate is them immersed in a charged solution of copper ions, such that the electrical pathways are formed by electrodeposition in the areas in the areas where the catalyst was placed.

These conventional methods are (i) time-consuming, (ii) expensive, (iii) wasteful of materials and (iv) productive of environmentally hazardous and toxic chemicals, primarily spent acids. Not only are numerous steps performed by skilled personnel necessary to produce a printed circuit board, but great amounts of conducting metal are needed for coating an entire dielectric substrate, or to provide an ionic solution.

2.3 Particular Conductive Ink Prior Art of Relevance to the Present Invention

2.3.1 First Feature - Metallic Particles

Yamazaki, U.S. Patent No. 4,696,764, discloses an electrically conductive adhesive composition having two types of electrically conductive particles with an average particle diameter of at least 1 micron (1 μ). The second type of particles need not be of the same material as the first, and has an average particle diameter of not more than 0.5 micron (.5 μ).

U.K. Patent Application GB 2054277 discloses a pressure-sensitive electroconductive elastic body of a matrix of electrically insulating material with a metal powder having particular densities, packing fraction, susceptibility to flow and bulk.

2.3.2 Second Feature - Metal Coating

Hasegawa et al., U.S. Patent No. 4,740,252, discloses a solder paste making use of conductive metallic particles which may be silver, nickel or copper. If copper is used, the patent discloses that the particles should be coated with nickel so as to make the surface wettable and to prevent formation of a brittle intermetallic compound on the surface of the particles.

Tsunaga et al., U.S. Patent No. 4,888.135, disclose an electrically conductive composition containing copper particles with a silver coating and a titanate coupling agent combined to the copper particles and/or the silver coating material.

Yamazaki et al., U.S. Patent No. 4,732,702, disclose an electroconductive resin paste comprising an epoxy resin formed from condensation of a bisphenol compound and a butadiene compound having carboxylic acid terminal groups and an electroconductive filler. The bisphenol compound may be a halogenated bisphenol A with epichlorohydrin.

2.3.3 General Interest

Japanese Patent 0133799, issued to Idea Research KK, discloses a conductive paint containing a mixture of binder (such as epoxy), conductive metal powder and solder. The abstract of the patent discloses that, when copper is the conductive metal, then a binder having flux function, such as epoxy-acrylic or phenol resin, is used to remove oxide film on the copper particles. This patent does not disclose the use of organic materials. An exemplary claim is directed to "conductive paint comprising, a mixture of metal powder and binder, characterized by: connecting said conductive metal powder to fused solder powder by way of heat treatment, said conductive metal powder and solder powder have a flake shape, uniformly mixing said composite of said conductive metal powder and said solder powder with said binder so as to form a low resistance conductor".

Japanese Patent 0160072, issued to Matsushita, discloses an electroconductive adhesive composition containing copper powder, solder powder. This patent also fails to disclose the use of organic materials. A first exemplary claim is directed to "conductive adhesive consisting of copper powder, solder powder, thermosetting resin, and activator". Dependent claims further define this conductive adhesive material as being characterized by: a weight ratio of the copper powder to the solder powder between the range from 10:5 to 10:1, and that the solder powder is in semi-molten state at the curing temperature of the thermosetting resin.

Japanese Patent Application JP 57-113505 also concerns a conductive ink. An exemplary claim is directed to "a conductive composition consisting of solder-plated copper powder, solder powder, an activating agent, and an organic resin". This conductive composition is characterized by a "weight ratio of the solder-plated copper powder to the solder powder in the range between 40:60 to 9:10".

Martin et al., U.S. Patent No. 4,564,563, disclose a solderable composition having silver flakes in a matrix formed of acrylic, vinyl and epoxy.

Tanaka et al., U.S. Patent No. 4,678,602, disclose a highly conductive styrene resin composition containing a copolymerized ...urated dicarboxylic acid anhydride and a metallic filler.

...akoshi et al., U.S. Patent No. 4,775,500 disclose a ...aking an electrically conductive polymeric composite ...ck as electrically conductive filler.

... Patent No. 4,786,437, discloses particle ... making use of pacifier, such as organotin ... bearing compounds, as an interfacial agent ...icles and a polymer matrix.

... Patent No. 4,830,[illegible] disclose an ...esin composition comprising a resin, a ...onic acid derivative and an alcohol.

... 4,874,548, discloses an ...e composition comprising an epoxy

United States Patent No. 5,376,403 issued December 27, 1994, for ELECTRICALLY CONDUCTIVE COMPOSITIONS AND METHODS FOR THE PREPARATION AND USE THEREOF is to Capote, et. al. including the selfsame Hugh Craig who is the inventor of the present invention. The Patent No. 5,376,403 concerns electrically conductive adhesive compositions, and methods for the preparation and use thereof, in which a solder powder, a chemically protected cross-linking agent with fluxing properties and a reactive monomer or polymer are the principal components. Depending upon the intended end use, the compositions comprise three or more of the following: a relatively high melting metal powder; solder powder; the active cross-linking agent which also serves as a fluxing agent; a resin; and a reactive monomer or polymer. The compositions are useful as improved conductive adhesives, such as for attaching electrical components to electrical circuits: the compositions comprising metal powder are ideally suited for creating the conductive paths on printed circuits. The compositions for forming conductive paths may first be applied to a substrate in the desired pattern of an electrical circuit, and then heated to cure it. During heating, the action of the cross-linking agent and optional reactive monomer or polymer within the mixture fluxes the metals, enabling sintering to occur between the metal powder and the solder powder.

2.4 <u>Dilemmas Encountered by Prior Art Conductive Inks</u>

2.4.1 <u>Conduction and Adhesion in Prior Art Conductive Inks</u>

Attempts to produce conductive inks over the course of a decade and longer have not as of yet met with commercial success. Among many other desirable attributes, a conductive ink must be, at a minimum, both highly and reliably (i) conductive and (ii) adherent.

To obtain good conductivity the metal particles in the conductive ink must be joined in molecular union. This not only typically requires a good, and strong, chemical flux, but good spatial mobility of the individual particles. This is because the particles must move and flow in order that the particles should join together integrally in the manner of a melting solder.

In order for a conductive ink to obtain good, reliable and permanent adherence to a substrate a strong and effective adhesive, such as an epoxy, is desired. The adhesive would normally "set up" or cure, at the same time and under the same conditions -- normally an elevated temperature -- as the metal particles are joining in molecular union to produce the desired circuit traces.

Herein lies a very great problem. The mobility of the metal particles, the fluxing agent, and any by-products of the fluxing would desirably be maximized so that a quality molecular metal film may be created with all residue of the chemical flux and any flux-borne contaminants and oxides borne to the surface of the film. Meanwhile, if the fluxing operation is not inherently hostile to the formation of an adhesive bond -- which it often is

-- the formation of an adhesive matrix serving to lock the metal particles in permanent position works against the requirement that these particle should be mobile so as to form a quality metal film, and circuit trace.

The "classic" problem with the production of printed circuits by conductive ink is, in the opinion of the inventor of the present invention, not simply that the chemistry of metal fluxing and adhesive-setting reactions is often at loggerheads, but that the physical requirements for the formation of metal films, and of adhesive bonds, are contradictory. The formation of an adhesive bond will desirably lock a metal particle, or metal matrix, in place (adhered to a substrate). In the curing of conductive inks this has been done simultaneously with the fluxing operation -- which demands mobility of the same metal particle. Accordingly, and although parameters of chemistry and process can be varied, so as to favor either the (i) conductive of (ii) adherent properties of the printed circuit traces so created, there is a tradeoff in the quality of (i) conductivity versus (ii) adhesion in the production of printed circuit traces, with traces that excel in one area often suffering in the other.

2.4.2 <u>Shelf Life of Prior Art Conductive Inks</u>

Conductive ink compositions have yet another, relatively more minor, problem. Conductive ink compositions of copper metallic powder and epoxy resins are unstable, and will gel within hours at room temperature. This short shelf life, or pot life, is a serious drawback for production operations producing printed circuit boards by the silkscreening of such conductive ink compositions. Copper conductive ink compositions in current use are commonly mixed from two components. When so mixed they have short useful life, and must be closely monitored in production use lest a product of varying, and/or unsatisfactory, quality should be produced.

Accordingly, it is an object of the present invention to provide improvements in the production of printed circuits. Another object of this invention is to provide a stable and consistent method for producing printed circuits quickly on a low-cost basis appropriate for both short and long production runs. Another object of this invention is to provide novel materials and associated apparatus for producing printed circuits by means of additive procedures. A further object of the invention is to provide improvements in printed circuits.

SUMMARY OF THE INVENTION

The present invention contemplates a method of making a conductive ink composition and the conductive ink so made, and a method of making printed circuits by use of the conductive ink composition and the printed circuits so made.

1. <u>A Conductive Ink Composition</u>

A conductive ink composition in accordance with the present invention consists essentially of (i) epoxy resin, (ii) metallic powders, and (iii) a polyacid serving both as a fluxing agent for the metallic powders and, in the presence of heat, as a curing agent for the epoxy resin.

More exactly, the relationship between these three components is quite sophisticated: The (iii) polyacid serves as a fluxing agent for the (ii) metallic powder so as to produce a metal oxide that is sufficient so as to, in the presence of heat, serve to catalyze a reaction between the (i) epoxy resin and the (iii) polyacid. Therefore, and although a simple acid could serve as a fluxing agent, a polyacid is necessary in the conductive ink composition of the present invention in order to cross-link two or more bonds of the epoxy resin.

Starting with the simplest component, the epoxy resin serves as adhesive. The preferred epoxy resin is typically either a diglcidyl ether of bisphenol A, or diglcidyl ether of BisOF.

The polyacid is either an organic dimer or trimer fatty acid with functionality greater than one or, preferably, a carboxyl-containing polymer. The organic dimer or trimer fatty acid having a functionality greater than one provides more than one reaction site with the epoxy resin, serving to create a macro-molecule that provides required adhesion. The preferred carboxyl-containing polymer also provides multiple reaction sites, as is well know in chemistry.

Both the preferred carboxyl-containing polymer, and, as an alternative, the organic dimer or trimer fatty acid, serve as a fluxing agent for the metallic powder, removing metal oxide from the metallic powder. This removal of the metal oxide permits the metal particles to sinter or coalesce, providing a continuous metallic conductor. Furthermore, the removed metal oxide is sufficient so as to, in the presence of heat, catalyze a reaction between the epoxy resin and the carboxyl groups on the polyacid.

The carboxyl-containing polymer is preferably a polycarboxcylic acid thermally stable at 215°C with an acid number >200 and a viscosity <10 centipoise, and is more preferably styrene acrylic acid copolymer. One (1) part of a mixture of the polyacid and the epoxy resin adhesive is mixed with approximately nine (9) parts, by weight, of metal powders. The preferred metal powders are (i) a highly-electrically-conducting, relatively-high melting temperature, oxidizable first metal powder in combination with a powder of an relatively-lower melting point alloy of both (ii) a second metal in combination with (iii) yet a third metal.

The first metal is typically drawn from the group consisting of copper (Cu), gold (Au), silver Ag), aluminum (Al), platinum (Pt), palladium (Pd), beryllium (Be), rhodium (Rh), nickel (Ni), cobalt (Co), iron (Fe), molybdenum (Mo), and/or high melting point alloys of these metals. The first metal is preferably copper powder in the range from 5 to 25 microns, and is nominally 10 micron copper.

The second metal is typically tin (Sn), lead (Pb), bismuth

(Bi), cadmium (Cd), zinc (Zn), gallium (Ga), indium (In), tellurium (Te), mercury (Hg), thallium (Tl), antimony (Sb), selenium (Se), polonium (Po), and/or alloys thereof. The second metal is preferably tin.

The third metal is preferably lead (Pb).

The second and third metals are combined as an alloy before making from them an alloy powder. The alloy powder is preferably tin-lead (Sn-Pb) eutectic alloy (Sn 63) in the range from 5 to 25 microns, and is nominally 10 micron powder.

2. <u>Use of the Conductive Ink Composition</u>

In considering the use of the conductive ink composition in accordance with the present invention all the following diverse chemical principles should be kept in mind: (i) the preferred tin/lead alloy is oxidizable, and has a lower melting temperature than the preferred copper; (ii) the preferred tin has, in its molten state, an affinity for the copper, (iv) the preferred tin and the preferred lead form, when melted together, a metal film, (v) the polyacid, preferably styrene acrylic acid copolymer, will flux both the copper an the tin/lead, and (vi) an oxide of the lead is a catalyst for a reaction between the epoxy resin adhesive and the polyacid (the styrene acrylic acid copolymer). Finally, and as is important in considering the stability (only) of the conductive ink, (vii) the copper powder catalyzes the reaction between the epoxy resin and the carboxyl resin, and this would desirably be eliminated or at least slowed at room temperature.

In use for the production of printed circuit boards the conductive ink is patterned on a dielectric substrate, normally by a screen printing process. The ink is heated, typically in an oven and preferably in vapor-phase oven that transfers heat quickly, to a temperature that is (i) above the lower melting temperature of the relatively-lower melting point alloy of the second metal and third metal (e.g., the tin/lead), but (ii) less than the relatively-higher melting temperature first metal (e.g., the copper), normally to 215°C for 5 minutes.

The metal powder (the copper) and the metal alloy powder (the tin/lead) are both strongly fluxed by the polyacid, permitting the molten tin to wet the surface of the copper. The tin/lead matrix becomes, in regions between the particles of copper, rich in lead. A molten metal film coalesces, expelling both the epoxy resin and the polyacid to the surfaces of the film. The epoxy resin now upon the surfaces of the metal film is catalyzed by the surface of the metal matrix which is now rich in lead oxide, becoming rapidly cured and cross-linked. Meanwhile all the polyacid groups are reacted with the epoxide groups so as neutralize the polyacid groups. A highly-electrically-conductive metal film strongly adhering to the dielectric substrate by a non-corrosive cured epoxy composition is produced.

3. <u>Philosophy and Appreciation of the Invention -- Synergism Between Conductive Ink Components</u>

What goes on in the curing of the conductive ink system in accordance with the present invention is, it is respectfully suggested, a minor miracle: the two flatly contradictory requirements of (i) a strong fluxing action which requires both a highly active reducing agent and a highly flowable low viscosity matrix, and (ii) reaction into the polymer resin of the system so as to both neutralize and immobilize the reducing environment, providing adhesion, are both met.

These contradictory requirements are met by the conductive ink composition of the present invention during the manufacture of printed circuits by synergism: (i) the acidic resin-adhesive component of the conductive ink serves as very effective chemical and mechanical flux for (ii) the metallic component of the same conductive ink, permitting the metallic component to coalesce as a metal film of excellent electrical and mechanical properties. During curing of the ink in a manner to be discussed, a metallic film coalesces with an oxide on its surface. This very oxide serves to catalyze a curing and a cross-linking of the resin-adhesive component, and a neutralizing of its acidity.

Ergo, each component promotes a change in the other component! The net result of this synergism between the resin-adhesive, and the metallic, components of the conductive ink composition is to produce a quality metal film that is strongly adhered to a dielectric substrate by a non-corrosive cured epoxy adhesive.

There is no wastage in the production of printed circuits with the conductive ink of the present invention, nor is there any emission of environmentally harmful liquids or gases. The conductive ink itself is safe, non-toxic and stable. The mechanical and electrical properties of electrical circuit traces produced with the conductive ink are fully the equal of normal (copper) printed circuit traces, typically exhibit conductivity of less than __ ohms per square. Accordingly, the thicknesses of the circuit traces produced need be no greater than normal (typically 6-10 microns), and no great quantity of the conductive ink is required. The conductive ink is, in any case, economical of (i) manufacture and (ii) use.

4. <u>Prolongation of the Shelf Life of Conductive Ink</u>

As still another aspect of the present invention, the stability and shelf life, or pot life, of conductive inks is greatly extended, typically by greater than an order of magnitude.

First, the metallic, normally copper, powder of the conductive ink is chelated with an organic coating, normally a benzatriazole, in order to provide an extremely thin coating on the individual particles of the powder. The coating retards oxide or salt formation. The same chelation of the copper also serves to desirably prevent the catalytic effect of the copper in promoting the cross-linking of the resin.

Second, an anti-oxidant copper deactivator, preferably oxalyl bis benzylidene hydrazine, is added to the resin to

beneficially further retard the cross-linking reaction of the resin. The preferred oxalyl bis benzylidene hydrazine material of the present invention exhibit an inhibitory effect in a copper-containing epoxy resins reacted with carboxylic resins by exhibiting a greater affinity for the inevitably-occurring copper salts than does the resin. Shelf life, or pot life, of copper-containing resin conductive ink is typically increased by more than an order of magnitude when the inhibitor is present in the resin in a preferred concentration in the range of .25% to 5%, and more preferably 1% by weight.

These and other aspects and attributes of the present invention will become increasingly clear upon reference to the following drawings and accompanying specification.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatic representation of a cross-section of un-sintered conductive ink in accordance with the present invention upon a substrate.

Figure 2 is a diagrammatic representation of a cross-section of sintered conductive ink in accordance with the present invention upon a substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Conventional printed circuits are made by what may best be described as a subtractive procedure in which circuit boards laminated with one or more conductive strata are etched to remove some portions of a conductive layer, leaving other portions, according to a predetermined circuit design. The technique involves relatively complex photographic procedures requiring large capital investments for etching and plating equipment and related apparatus, such as cameras and the like. In general, the time required to design and produce a printed circuit with conventional techniques is quite long and requires a number of skilled technicians. As a result, relatively few companies are capable of producing printed circuits using conventional techniques. Also, because of the time and expense involved in preparing a printed circuit, standard procedures are not appropriate for short production runs, even though the printed circuit may otherwise be desirable.

1. <u>Preferred Composition of the Conductive Ink of the Present Invention</u>

In accordance with a first aspect of the present invention, a conductive ink composition is made from an (i) acidic resin-adhesive component and a (ii) metallic component. The acidic resin-adhesive component consists essentially of (i) a resin-adhesive component and (ii) a polyacid component.

The resin-adhesive component typically consists essentially

of an epoxy resin adhesive. The epoxy resin adhesive is typically a diglcidyl ether of bisphenol A, or diglcidyl ether of BisOF.

The polyacid component is preferably a carboxyl-containing polymer, is more preferably a polycarboxylic acid. Among polycarboxylic acids long-chain aliphatic dimers and/or trimers of fatty acids, or a carboxyl-containing polymer, are preferred, with the carboxyl-containing polymer being most preferred. The less-preferred dimers or trimers of fatty acids are preferably dimers or timers of any of palmitic, stearic, oleic and/or linoleic acids. The more-preferred carboxylated polymer is preferably an acrylic acid copolymer, and is still more preferably styrene acrylic acid copolymer.

The resin-adhesive component is joined with the polyacid component by the simple expedient of mixing the two components together.

Before curing, and during the preparation of the conductive ink, the acidic resin-adhesive mixture (and the optional exothermic compound, if present -- see the next section) is mixed with typically two metal/metal alloy powders. A powder of a first metal is (i) highly electrically conducting, (ii) possessed of a relatively high melting temperature, and (iii) subject to oxidation. The first metal is typically either copper (Cu), gold (Au), silver Ag), aluminum (Al), platinum (Pt), palladium (Pd), beryllium (Be), rhodium (Rh), nickel (Ni), cobalt (Co), iron (Fe), molybdenum (Mo), and/or high melting point alloys of these metals. The first metal is preferably 10 micron copper.

A powder of a metal alloy includes at least a second metal and a third metal. The metal alloy is (i) subject to oxidation and (ii) possessed of a relatively low melting temperature that is less than the melting temperature of the first metal. The second metal component of the metal alloy has, in its molten state, an affinity for the first metal. Meanwhile, an oxide of the third metal is catalyst for the curing of the epoxy resin adhesive. Finally, the second metal and the third metal form, when melted together, a metal film. The second metal is typically tin (Sn), lead (Pb), bismuth (Bi), cadmium (Cd), zinc (Zn), gallium (Ga), indium (In), tellurium (Te), mercury (Hg), thallium (Tl), antimony (Sb), selenium (Se), polonium (Po), and/or alloys thereof. The second metal is preferably tin. The third metal is also either tin (Sn), lead (Pb), bismuth (Bi), cadmium (Cd), zinc (Zn), gallium (Ga), indium (In), tellurium (Te), mercury (Hg), thallium (Tl), antimony (Sb), selenium (Se), polonium (Po), and/or alloys thereof. The third metal is preferably lead, making that the oxide of the third metal is quite obviously lead oxide.

The preferred tin/lead alloy is preferably of a particle size of 25 microns or smaller, and is preferably of less than 10 microns size. The acidic epoxy adhesive component (and any optional exothermic compound component) of the conductive ink is typically from 2% to 20% of the conductive ink by weight, and the metal and metal alloy powders are typically from 98% to 80% by

weight. The acidic epoxy adhesive component is more preferably approximately 20% of the conductive ink by weight, and the metal and metal alloy powders are more preferably approximately 80% by weight.

Of suitable metal and metal alloy powders, the higher-melting-point highly-electrically-conductive first metal (nominally copper) is preferably from 51% to 90% by weight, and is more preferably 60% Meanwhile the metal alloy powder of the combined second and third metals jointly (nominally tin and lead) is preferably from 49% to 10% by weight, and is more preferably 40%.

Still further in accordance with the present invention, the stability of conductive inks during storage and use is maintained for longer times then heretofore. The improved stability helps alleviate quality problems in production of printed circuits with the inks. In accordance with the present invention, improved stability is imparted in either of two ways.

First, the metallic, normally copper, powder is chelated with an organic coating, normally a benzatriazole, in order to provide an extremely thin coating on the individual particles of the powder. This coating neither detracts from the electrical conductivity, nor degrades the solder wetting characteristics, of the powder. Such triazole coatings are well known in the art as a means of preventing oxide formation on copper materials, and are commonly used to maintain the solderability of copper lands on printed circuit boards. Triazole coatings have also been used in copper powder paints to reduce oxidation and to maintain electrical conductivity when conductivity is dependent upon physical contact of the individual metal particles of the powder (since oxide formation reduces conductivity).

However, in the present invention the chelation of the copper is also used to prevent the catalytic effect of the copper in promoting the cross-linking of the resin -- providing thereby an additional benefit.

Second, a novel anti-oxidant copper deactivator is added to the resin to provide a "second front" against the catalyst. A preferred deactivator is oxalyl bis benzylidene hydrazine. Copper deactivators, including the preferred oxalyl bis benzylidene hydrazine, have previously found commercial application in preventing embrittlement of polyethylene hook-up wire when it comes into contact with copper metal. This embrittlement was caused by an oxidative cross-linking and degrading of the polymer by copper salts. However, no previous use of a copper deactivator in combination with epoxy resin is known to the inventor.

The preferred oxalyl bis benzylidene hydrazine material of the present invention exhibit an inhibitory effect in a copper-containing epoxy resins reacted with carboxylic resins. The inhibitor so serves by exhibiting a greater affinity for the copper salts than does the resin. Shelf life, or pot life, of copper-containing resin conductive ink is typically increased by more than an order of magnitude when the inhibitor is present in

substantial contamination of any nature whatsoever.

The sintered metal is located where it is desired to be; namely in the traces between electrically-connected points. The metal is of excellent quality.

The cured resin adhesive is located where it is desired to be; namely between the metal traces and the substrate so as to adhere such traces strongly to the substrate, and also on the opposite side of the metal traces where it serves to protect the traces against chemical and even physical degradation. The cured resin adhesive is of excellent quality.

Ergo, printing of quality printed circuit boards with conductive ink has been realized.

3. <u>Preferred Compositions of Optional Coatings and/or Exothermic Agents Susceptible of Combination With The Conductive Ink of the Present Invention</u>

The most-preferred carboxylated polymer of the conductive ink of the present invention may, in particular, be coated with and organic materials, preferably polymeric fluxing adhesive, so as to accept and hold static electric charge so that it, and the entire conductive ink composition of which it is a part may be electrostatically imaged, particularly for the direct computer-to-plate imaging of printed circuit boards by a laser printer -- but this is the subject of another, related patent application.

A compound undergoing a exothermic reaction in the presence of metals is optionally included. One preferred such compound is adipic acid dihydrazide.

Save for the addition of the optional exothermic compound, the reaction of the (i) resin-adhesive and (ii) acid components to cure the resin-adhesive is at a temperature of typically at least 200°C for a period of typically at least __ minutes. This temperature typically requires that, for maximum reliability, the dielectric substrate upon which the conductive ink is printed, and subsequently cured, should be made of ceramic or epoxy glass. While this is by no means an unacceptable limitation, the low cost of the conductive ink, and the efficient method of imaging the conductive ink (by printing, and by curing), so as to produce, in accordance with the present invention, printed circuit boards make it desirable that the most inexpensive dielectric substrates -- such as molded thermoplastic, phenolic, and even polyester -- should be usable.

Use of these "low temperature" substrates, and others, is enabled by the optional inclusion of the exothermic compound, preferably adipic acid dihydrazide, which undergoes an exothermic reaction during curing. This exothermic reaction adds approximately 40°C locally at the conductive ink traces (which are the only locations required to be cured). The overall temperature of the oven within which the conductive ink is cured may thus be lowered to less than 160°C.

A conductive ink in accordance with the present invention consists essentially of an epoxy resin, carboxylated resin and metallic powders in a solvent. The conductive ink is suitably

(i) printed on a dielectric substrate in some predetermined circuit design pattern, and then, as patterned, (ii) elevated in temperature. The metallic powders are fluxed by acid, and coalesce into a metal film having any desired conductivity. The poly acid and the epoxy resin are expelled to the exterior of the metal film. The metal film catalyzes the curing and bonding of the epoxy resin. The acid is neutralized. There is no wasted material in the process, nor any environmentally detrimental gaseous or liquid emission or by-product.

In accordance with the present invention, an epoxy resin, preferably a thermosetting epoxy resin, is loaded with conductive metal powders, preferably and primarily powdered copper. The conductive metal powder is of a mesh size suitable to the resolution of any pattern to which the ink will be printed, normally smaller than 200 mesh and preferably as small as 325 mesh and smaller. Silver or gold may be substituted for the copper at increased cost of material. Nickel may also be substituted for the copper at the cost of reduced electrical conductivity in electrical circuit traces produced with the conductive ink.

The epoxy resin is also loaded with solder in powder form, normally a lead-tin alloy solder and preferably a powdered mixture of approximately 60% lead and 40% tin by weight. The powdered solder may also include antimony. It is irrelevant and of no use to the process of present invention, and it is correspondingly not desired (although it is not prohibited), that the solder powder should be suspended in a binder, and/or that it should be combined with a strong fluxing agent.

The epoxy resin and the metallic powders -- typically copper, lead and tin in a nominal ratio of 6 to 1 to 2 by weight -- are combined with the resins. In overall composition, the conductive ink is preferably 5% epoxy., 5% poly acid, and 90% metals, by weight.

In use for manufacturing printed circuits, the conductive ink is printed on a dielectric substrate in some predetermined circuit design. The pattern ink upon the substrate is then heated, normally and preferably in a vapor phase oven, to a temperature greater than the melting point of at least one of the metallic powders, normally to approximately 210° Centigrade which is greater than the melting points of both lead and tin. The acid serves as a fluxing agent to the oxidizable copper powder, removing oxide from the surface of the copper particles and permitting the molten tin, which has an affinity for copper, to wet the surfaces of the copper particles. As the tin is attracted to the surfaces of the copper particles the matrix of the molten tin and lead becomes, in regions between the wetted particles of copper, rich in lead.

A metal film of tin and lead in which film is embedded copper particles is formed. This metal film drives out the epoxy/acid resin to its exterior surface, including the surface whereat exists the dielectric substrate. The epoxy upon the surfaces of the metal film is cross-linked by a catalyzed

reaction to the substrate, and cured.

The net result is to form (i) a patterned metallic film that is electrically conductive by virtue of the copper particles contained therein, with (ii) a cured epoxy upon the surfaces of the electrically-conductive metal film which cured epoxy serves to strongly bond the film to the underlying substrate.

In accordance with the preceding explanation, variations and adaptations of the conductive ink composition in accordance with the present invention will suggest themselves to a practitioner of the chemical engineering arts.

In accordance with these and other possible variations and adaptations of the present invention, the scope of the invention should be determined in accordance with the following claims, only, and not solely in accordance with that embodiment within which the invention has been taught.

CLAIMS

What is claimed is:

1. A conductive ink composition consisting essentially of
epoxy resin;
metalllic powders; and
a polyacid serving both as a fluxing agent for the metallic powders and, in the presence of heat, as a curing agent for the epoxy resin.

2. The conductive ink composition according to claim 1 wherein the polyacid is from the group consisting essentially of:
a carboxyl-containing polymer; and
an organic hydrazide
with functionality greater than one.

3. The conductive ink composition according to claim 2 wherein the polyacid is thermally stable to 215°C with an acid number greater than 200 and with viscosity less than 10 centipoise at 200°C.

4. The conductive ink composition according to claim 1 wherein the polyacid consists essentially of
a carboxyl-containing polymer serving as a fluxing agent for the metallic powder so as to produce a metal oxide that is sufficient so as to, in the presence of heat, serve as a catalyst for reaction between the epoxy resin and the carboxyl.

5. The conductive ink composition according to claim 4 wherein the carboxyl-containing polymer is drawn from the group consisting of:
carboxylated polymers;
polycarboxcylic acid; and
polymer fatty acids.

6. The conductive ink composition according to claim 4 wherein the carboxyl-containing polymer consists essentially of:
polycarboxcylic acid

7. The conductive ink composition according to claim 6 wherein the polycarboxcylic acid consists essentially of:
styrene acrylic acid copolymer.

8. The conductive ink composition according to claim 1 wherein the metallic powders are from the group consisting of
a high-melting-point highly-electrically-conductive metal; and
a low-melting-point metal.

9. The conductive ink composition according to claim 8 wherein the metallic powders are by weight percent

from 20% to 80% high-melting-point highly-electrically-conductive metal; and

from 80% to 20% low-melting-point metal.

10. The conductive ink composition according to claim 8 wherein the high-melting-point highly-electrically-conductive metal is a metal from the group consisting of

copper (Cu);
gold (Au);
silver Ag);
aluminum (Al);
platinum (Pt);
palladium (Pd);
beryllium (Be);
rhodium (Rh);
nickel (Ni);
cobalt (Co);
iron (Fe);
molybdenum (Mo); and
high melting point alloys of these metals.

11. The conductive ink composition according to claim 8 wherein the low-melting-point metal is from the group consisting of

tin (Sn);
lead (Pb);
bismuth (Bi);
cadmium (Cd);
zinc (Zn);
gallium (Ga);
indium (In);
tellurium (Te);
mercury (Hg);
thallium (Tl);
antimony (Sb);
selenium (Se);
polonium (Po); and
alloys thereof.

12. The conductive ink composition according to claim 1 wherein the metallic powders are of size less than 25 microns.

13. The conductive ink composition according to claim 1 wherein the epoxy resin consists essentially of

a low viscosity liquid epoxy resin.

14. The conductive ink composition according to claim 1 wherein the conductive ink composition is by weight percent

between 5% and 25% epoxy resin and carboxyl-containing polymer, jointly; and

between 95% and 75% metallic powders. —

15. A conductive ink composition consisting essentially of
an epoxy resin curable by heat in the presence of a metal oxide;
metallic powders; and
a carboxyl-containing polymer serving as a fluxing agent for the metallic powder so as to produce a metal oxide that is sufficient so as to, in the presence of heat, serve to catalyze a reaction between the epoxy resin and the carboxyl.

16. The conductive ink composition according to claim 15 wherein the carboxyl-containing polymer is drawn from the group consisting of
carboxylated polymers; and
fatty acids.

17. The conductive ink composition according to claim 15 wherein the carboxylated polymers consist essentially of:
polycarboxylated polymers;
and wherein the fatty acids consist essentially of:
dimers or trimers of fatty acids.

18. The conductive ink composition according to claim 15 wherein the metallic powders are from the group consisting of
a high-melting-point highly-electrically-conductive metal; and
a low-melting-point metal.

19. A conductive ink composition consisting essentially of
an epoxy resin adhesive;
a carboxyl-containing polymer; and
a powder of a great multiplicity of particles of a highly-electrically-conducting first metal,
which first metal has a first melting temperature, and
which first metal is subject to oxidation;
a powder of a great multiplicity of particles of a metal alloy including at least a second metal and a third metal,
which metal alloy is subject to oxidation,
which metal alloy has a second melting temperature less than the first melting temperature,
which second metal has in its molten state an affinity for the first metal,
an oxide of which third metal is catalyst for the curing of the epoxy resin adhesive, and
which second metal and which third metal when melted together form a metal film; and
wherein when the conductive ink composition is heated to a temperature above the second temperature but less than the first temperature then
the carboxyl-containing polymer serves as a fluxing agent to the oxidizable first metal powder and also to the oxidizable metal alloy powder, removing oxide from the surface of particles of the first metal and also of the metal alloy, so as

to permit

the molten second metal to wet the surface of the first metal to which first metal it has an affinity, while

a matrix of the second and the third molten metals becomes, in regions between the particles of first metal, rich in the third metal, while

a molten metal film of the second and the third metals in which film is embedded particles of the first metal coalesces, so that

the metal film extrudes both the epoxy resin and the carboxyl-containing polymer to its surfaces, so that

the epoxy resin is upon the surfaces of the metal film is catalyzed by the matrix rich in oxide of the third metal, becoming rapidly cured and cross-linked, while

all the carboxyl-containing polymer is reacted with the epoxide groups so as neutralize the acid groups,

wherein a film that is highly electrically conductive by virtue of the particles of the first metal contained therein is adhered to the substrate by a non-corrosive cured epoxy composition.

20. A method of making an electrically conductive circuit on a dielectric surface comprising:

patterning the circuit upon a dielectric surface by printing the dielectric surface with an electrically conductive ink composition consisting essentially of

an epoxy resin adhesive,

a carboxyl-containing polymer, mixed with

a powder of a highly-electrically-conducting oxidizable first metal having a first melting temperature, and

a powder of an oxidizable alloy of

a second metal having an affinity for the first metal, and

a third metal that is a catalyst to any curing of the epoxy resin adhesive,

which alloy has a second melting temperature less than the first melting temperature, and

which third metal and which second metal form, when melted together, a metal film;

heating the conductive ink composition patterned upon the dielectric surface to a temperature above the second temperature but less than the first temperature so that

the carboxyl-containing polymer serves as a fluxing agent to the oxidizable first metal powder and to the alloy powder, removing oxide from the surface of the first metal powder and also from the alloy powder so as to permit

the molten second metal to wet the surface of the first metal, meanwhile that

the matrix of the second and the third molten metals becomes, in regions between the particles of first metal, rich in the third metal, and

a metal film of the second and the third metals in

which film is embedded particles of the first metal coalesces, where

the metal film extrudes the epoxy resin and the carboxyl-containing polymer to its surfaces, so that

the epoxy resin that is upon the surfaces of the metal film is catalyzed by the matrix rich in oxide of the third metal, becoming rapidly cured and cross-linked, while

all the carboxyl-containing polymer is reacted with the epoxide groups so as neutralize the acid groups; and

cooling the conductive ink with its coalesced metal film, its cured and cross-linked epoxy resin adhesive, and its neutralized acid;

wherein an electrical circuit that is highly electrically conductive by virtue of the particles of the first metal contained in the metal film is patterned upon the substrate and adhesively adhered thereto by a non-corrosive cured epoxy resin adhesive.

21. The method of making an electrically conductive circuit on a dielectric surface according to claim 20 wherein the patterning comprises:

printing the dielectric surface with the electrically conductive ink composition by process of silkscreening.

22. An electrically conductive circuit made in accordance with the method of claim 20 CHARACTERIZED IN THAT

a metal film, within which film particles of a highly-electrically-conductive first metal are coated with a second metal within a metal alloy matrix that is rich in a third metal, is patterned upon a substrate and adhesively adhered thereto by a non-corrosive cured and cross-linked epoxy resin adhesive.

23. An electrically conductive circuit upon a dielectric substrate comprising:

a patterned metal film consisting essentially of

particles of a highly-electrically-conductive first metal, coated with

a second metal having an affinity to the first metal, embedded within

a metal alloy matrix that is rich in a third metal; and

a non-corrosive cured and cross-linked epoxy resin adhesive, located upon the surfaces of the metal film, for bonding the metal film to the substrate;

wherein there is no appreciable amount of the epoxy resin adhesive, nor any acid, within the patterned metal film; and

wherein there is no appreciable amount of any of the first, second or third metals, nor any acid, within the epoxy resin adhesive.

24. The electrically conductive circuit according to claim 23 wherein the patterned metal film consists essentially of

first metal particles from the group consisting of copper

(Cu), gold (Au), silver Ag), aluminum (Al), platinum (Pt), palladium (Pd), beryllium (Be), rhodium (Rh), nickel (Ni), cobalt (Co), iron (Fe), molybdenum (Mo), and alloys of these metals; coated with

second metal particles from the group consisting of tin (Sn), lead (Pb), bismuth (Bi), cadmium (Cd), zinc (Zn), gallium (Ga), indium (In), tellurium (Te), mercury (Hg), thallium (Tl), antimony (Sb), selenium (Se), polonium (Po), and alloys thereof; embedded within

a metal matrix that is rich in lead.

25. The conductive ink composition according to claim 23 wherein the particles of a highly-electrically-conductive first metal consist essentially of

copper; and

wherein the second metal having an affinity to the first metal consists essentially of:

tin; and

wherein the metal alloy matrix consists essentially of

lead.

26. A stability enhancer for a conductive composition including copper powder and carboxyl-cured epoxy resin, the stability enhancer consisting essentially of

an organic chelation agent;

wherein stability is enhanced by coatings of the copper powder by process of chelation.

27. The stability enhancer according to claim 26 wherein the organic chelation agent consists essentially of:

benzatriazole.

28. The stability enhancer according to claim 26 wherein the organic chelation agent that, in addition to the organic chelation agent, consists essentially of:

an anti-oxidant copper deactivating agent;

wherein stability is further enhanced by retarding across-linking reaction of the resin.

29. A stability enhancer for a conductive composition including copper powder and carboxyl-cured epoxy resin, the stability enhancer consisting essentially of

an anti-oxidant copper deactivating agent.

30. The stability enhancer according to claim 29 wherein the anti-oxidant copper deactivating agent consists essentially of:

oxalyl bis benzylidene hydrazine.

31. The stability enhancer according to claim 29 wherein the organic chelation agent that, in addition to the organic chelation agent, consists essentially of:

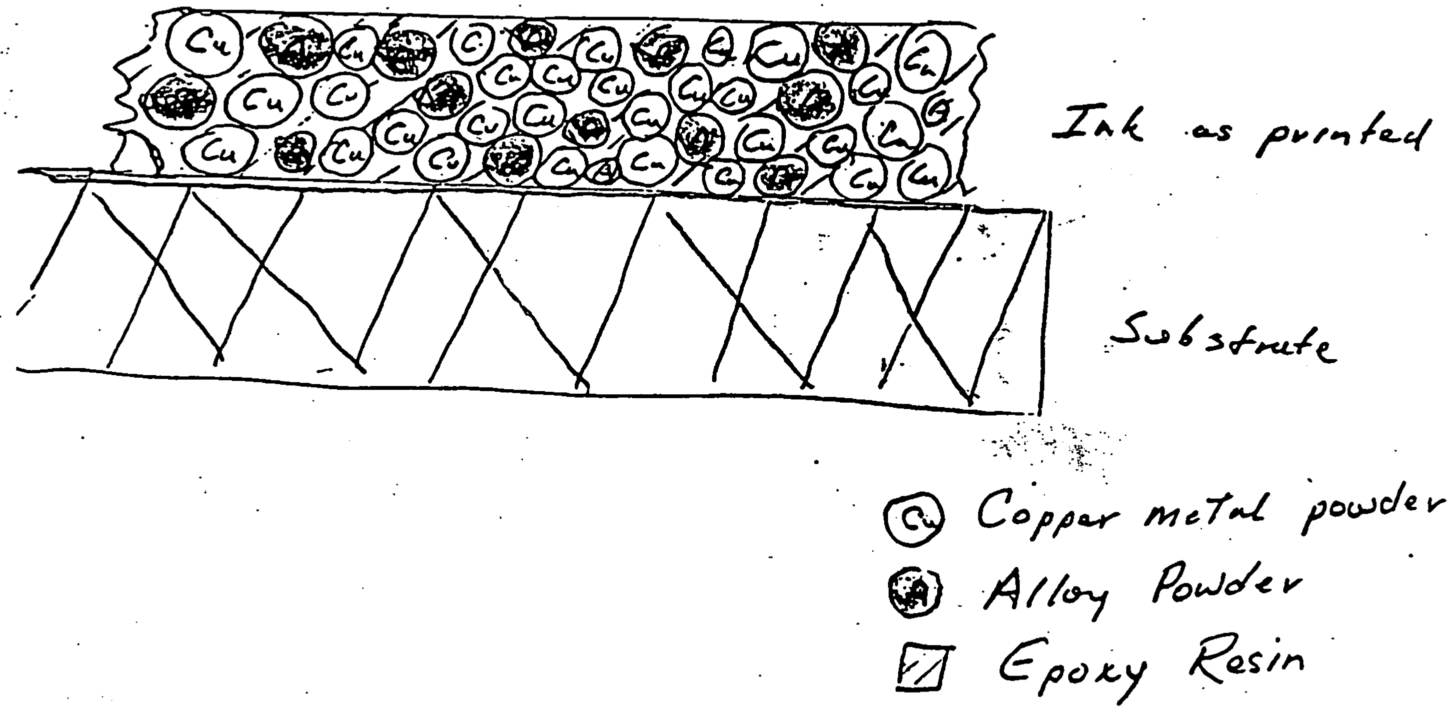
an anti-oxidant copper deactivating agent;

wherein stability is further enhanced by retarding across-linking reaction of the resin.

ABSTRACT

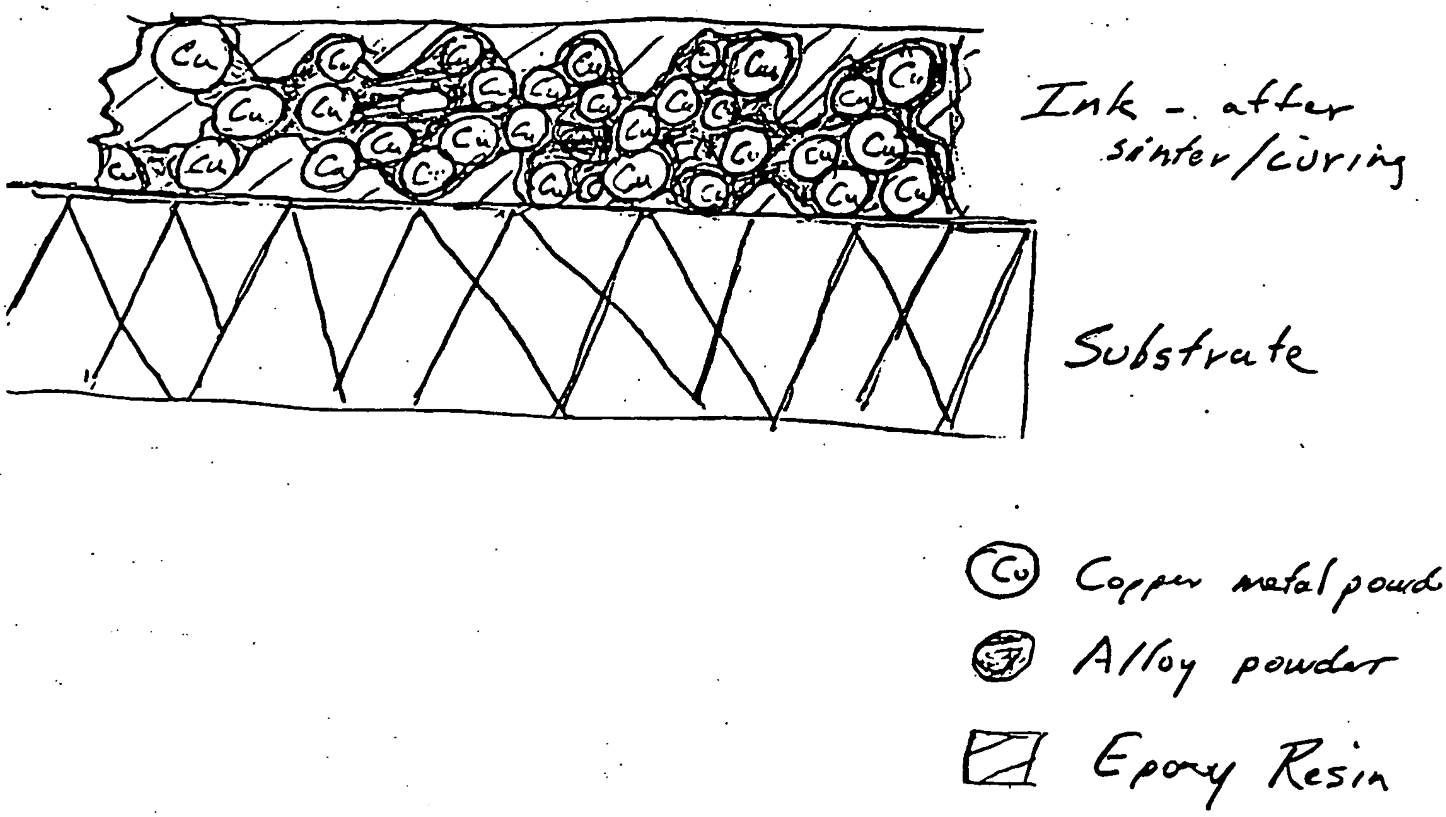
An epoxy resin is reacted with a polyacid, permissively a long-chain aliphatic dimer/trimer fatty acid but preferably a carboxyl-containing compound and more preferably a polycarboxcylic acid thermally stable to 215°C with an acid number >200 and a low viscosity <10 centipoise, most preferably styrene acrylic acid copolymer. One part of the resulting acidic epoxy resin adhesive is mixed with nine parts, by weight, of (i) a highly-electrically-conducting, relatively-high melting temperature, oxidizable first metal powder -- preferably 10 micron copper -- and (ii) a powder of an alloy of both a second metal -- preferably tin -- in combination with a third metal -- preferably lead. The conductive ink is patterned on a dielectric substrate, normally by screen printing, and heated, normally 215°C for 5 minutes. The copper and tin/lead are strongly fluxed by the polyacid, permitting the molten tin to wet the surface of the copper. The tin/lead matrix becomes, in regions between the particles of copper, rich in lead. A molten metal film coalesces, expelling both the epoxy resin and the styrene acid copolymer to the surfaces of the film. The epoxy resin now upon the surfaces of the metal film is catalyzed by the surface of the metal matrix which is now rich in metal oxide, becoming rapidly cured and cross-linked. All polyacid groups are reacted with the epoxide groups so as neutralize the polyacid groups. A highly-electrically-conductive metal film strongly adhering to the dielectric substrate by a non-corrosive cured epoxy composition is produced.

Fig. 1



Cross section of unsintered ink on substrate

Fig 2



Cross section of Sintered Ink on Substrate

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Hugh Craig

Docket No.: SVT 0001P

Title: CONDUCTIVE INK COMPOSITION, AND ENVIRONMENTALLY-SAFE METHOD OF PRINTING AND CURING SAME ON DIELECTRIC SURFACES FOR THE MANUFACTURE OF PRINTED CIRCUIT BOARDS

VERIFIED STATEMENT UNDER 37 CFR §1.27 OF STATUS AS A SMALL ENTITY

I, Hugh Craig, an individual, hereby declare that:

1. I am an independent inventor.

2. I am the inventor named in the above-identified provisional patent application entitled **CONDUCTIVE INK COMPOSITION, AND ENVIRONMENTALLY-SAFE METHOD OF PRINTING AND CURING SAME ON DIELECTRIC SURFACES FOR THE MANUFACTURE OF PRINTED CIRCUIT BOARDS** and am the owner of said provisional patent application and invention.

3. I qualify as an independent inventor as defined in 37 CFR §1.9, Subsection (c) in that I a) have not assigned, granted, conveyed or licensed, and b) am under no obligation under contract or law to assign, grant, convey or license any rights in the invention to any person who could not likewise be classified as an independent inventor if that person had made the invention, or to any concern which would not qualify as a small business concern or a non-profit organization under said §1.9.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

August 16, 1996
Date

Hugh P. Craig
Signature of Hugh Craig

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference HL55521/002	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IB 97/01033	International filing date *(day/month/year)* 15/08/1997	(Earliest) Priority Date *(day/month/year)* 16/08/1996
Applicant CRAIG, Hugh P.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title**,
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

   Figure No. 3
   - [ ] as suggested by the applicant.
   - [X] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/01033

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H05K1/09 H05K3/12 H01B1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05K H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 376 403 A (CAPOTE ET AL.) 27 December 1994 cited in the application see column 4, line 1 - column 13, line 15 ---	1-6,20, 21, 29-37, 43, 50-53,58
A	WO 95 13901 A (CTS CORPORATION) 26 May 1995 see page 11, line 17 - page 13, line 12 ---	1-5,20, 21, 29-34,53
A	WO 96 13041 A (SOLAIC) 2 May 1996 see the whole document --- -/--	1-5,20, 29-36, 43,50

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
11 November 1997	08/12/1997
Name and mailing address of the ISA	**Authorized officer**
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Mes, L

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 35 (C-046), 5 March 1981 & JP 55 160072 A (MATSUSHITA ELECTRIC IND CO), 12 December 1980, cited in the application see abstract ---	1-5,20, 21,29-34
A	DATABASE WPI Week 7901 Derwent Publications Ltd., London, GB; AN 79-01104B XP002046421 & JP 53 133 799 A (IDEA RES KK) , 21 November 1978 cited in the application see abstract ---	1-5,20, 21,29-34
A	WO 96 22670 A (COATES BROTHERS PLC) 25 July 1996 see page 5 - page 15 ---	20,22, 29-35, 43-46, 48,49
A	US 3 915 729 A (EUSTICE) 28 October 1975 see abstract ---	6,25-27
A	US 4 663 079 A (YAMAGUCHI ET AL.) 5 May 1987 see abstract ---	13-17, 38-40
P,A	WO 96 30966 A (LITTON PRECISION PRODUCTS INTERNATIONAL) 3 October 1996 see the whole document -----	20-23, 29-35, 43,44

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 97/01033

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5376403 A	27-12-94	AU 663342 B	05-10-95
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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference WS/1-1L55521002	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
International application No. PCT/IB97/01033	International filing date *(day/month/year)* 15/08/1997	Priority date *(day/month/year)* 16/08/1996
International Patent Classification (IPC) or national classification and IPC H05K1/09		
Applicant CRAIG, Hugh P.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 31 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   VI ☐ Certain documents cited
   VII ☒ Certain defects in the international application
   VIII ☒ Certain observations on the international application

Date of submission of the demand 26/01/1998	Date of completion of this report 16. 11. 98
Name and mailing address of the IPEA/ European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Ketterl, F Telephone No. (+49-89) 2399-2467

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-4,6,20,25, 27-36	as originally filed			
5,7-19,19a,21-24, 26	as received on	16/09/1998	with letter of	15/09/1998

Claims, No.:

1-56	as received on	16/09/1998	with letter of	15/09/1998

Drawings, sheets:

1/2,2/2	as received on	03/10/1997	with letter of	01/10/1997

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-56
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-56
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-56
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

CONCERNING SECTION V:

The following comments assume that the lack of clarity of claims 1 and 18 outlined in Section VIII is overcome by a clear definition of the crosslinking agent and the polycarboxyl compound, respectively, as being selected from carboxylated polymers, polycarboxylic acids or polymer fatty acids, so as to provide multiple reaction sites.

1). The composition of matter of claim 1 meets the requirements of Article 33 (2) to (4) PCT. The reasons are as follows:

- As the closest prior art reference, US,A,5 376 403 (hereinafter referred to as D1) has to be taken into account. From this document, there is known (see column 5, lines 16 to 60, column 6, lines 11 to 63, column 7, line 16 to column 8, line 11, column 8, line 29 to column 9, line 2 and column 10, lines 33 to 48) a composition comprising a metal powder, a lower melting solder powder, an epoxy based crosslinkable polymer, and a polyanhydride, e.g. phthalic anhydride based crosslinking agent. The latter is provided with protecting or inhibiting groups at the anhydride, has fluxing properties and is non-reactive with the polymer without the application of heat. As a consequence of the presence of an oxide surface on the particles of the metal powder, the composition also comprises metallic oxide catalysts which promote a rapid crosslinking reaction between the polymer and the cross-linking agent.

  From the known composition, the claimed one differs in that the crosslinking agent is selected from carboxylated polymers, polycarboxylic acids or polymer fatty acids. These agents do not crosslink under storage conditions, but only upon application of heat and provision of catalysts, thereby avoiding the application of protecting groups.

  There is no suggestion in the cited prior art to select these crosslinking agents. Hence the claimed composition involves an inventive step.

2). For analogous reasons, the composition of claim 18 fulfills the requirements of Article 33 (2) to (4) PCT. In this case, the necessity of protecting groups is avoided by selecting crosslinking agents which are bifunctional in that they act as

a fluxing agent at a first temperature and as a crosslinking agent at a second, higher temperature.

The use of such crosslinking agents is not suggested by the cited prior art. Therefore, the claimed composition involves an inventive step.

3). Dependent claims 2 to 17 and 19 to 39 refer to special embodiments of the compositions of claims 1 and 18, respectively, and therefore also involve an inventive step. Hence the requirements of Article 33 (2) to (4) PCT are likewise met.

4). The methods of claims 40 to 56 make use of the above compositions and therefore also involve an inventive step. Consequently, the requirements of Article 33 (2) to (4) are met.

CONCERNING SECTION VII:

1). The description in the paragraph linking pages 11 and 12 is not harmonized with the claims. Thus, the requirements of Rule 5.1(a)(iii) PCT are not met.

CONCERNING SECTION VIII:

1). Claims 1 and 18 lack clarity and therefore do not meet the requirements of Article 6 PCT. The rasons are as follows:

1.1 The definition of the crosslinking agent in claim 1 is unclear, since it only recites its desired performance in the composition, rather than indicating the compounds as such by which these requirements are met. Such a definition could only be considered as being clear if the agents showing this performance are obvious to a skilled person. This condition does not appear to be met in the present case.

1.2 The above objection analogously applies to the definition of the polycarboxyl compound in claim 18, which merely recites the desired properties of the

polycarboxyl compound at different temperatures. This way of claiming could only be considered as being clear in case that the compounds showing these properties are obvious to a skilled person. This condition is, however, not fulfilled in the present case.

1.3 Claim 18 further is ambiguous as to whether the epoxy resin is a component of the claimed composition, or the polycarboxyl compound is defined in terms of its relation to the epoxy resin without the latter being a component of the composition. In the latter case, a further lack of clarity has to be stated, since the claim fails to define the components in terms of their substantial features.

1.4 Moreover, the present wording of claims 1 and 18 using the non-limiting term "comprising" and different definitions of the crosslinking agent and the polymer leads to a doubt what in fact are the essential features of the invention, taking into account the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT that any independent claim must contain **all** the technical features essential to the definition of the invention.

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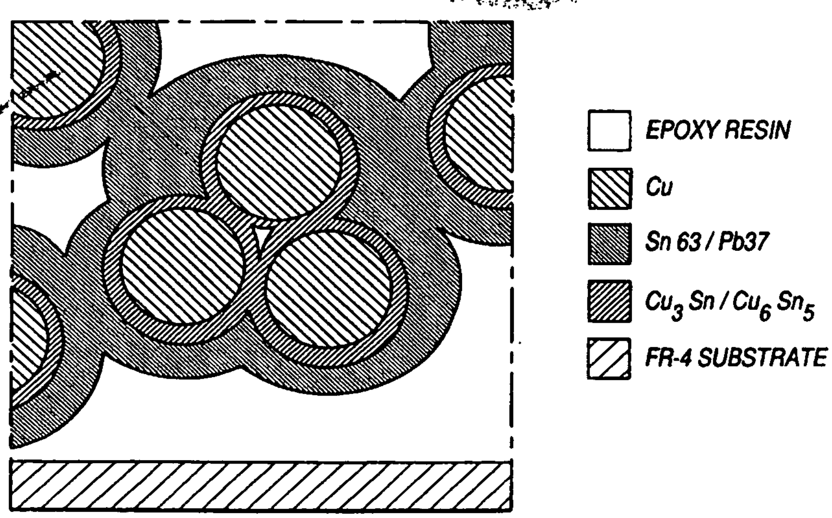
(54) Title: PRINTABLE COMPOSITIONS, AND THEIR APPLICATION TO DIELECTRIC SURFACES USED IN THE MANUFACTURE OF PRINTED CIRCUIT BOARDS



(57) Abstract

A composition for use in the production of metal traces and other metal components of printed circuit boards, wiring boards and the like comprises the following components: (a) a metal powder, (b) a solder powder, (c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being cross-linkable under the action of a chemical cross-linking agent, and (d) a chemical cross-linking agent for said polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis. The polymer will generally be an epoxy resin and the cross-linking agent will generally be a polyacid. The composition preferably is one in which the metal powder and/or solder powder generates and/or has adhered thereto a catalyst for the cross-linking agent which is liberated on application of heat.

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U.S. Patent No. 4,775,500 discloses a method of making an electrically conductive polymeric composite with carbon black as electrically conductive filler.

U.S. Patent No. 4,786,437 discloses particle filled compositions making use of a pacifier, such as an organotin compound or sulphur bearing compounds, as an interfacial agent between conductive particles and a polymer matrix.

U.S. Patent No. 4,830,779 discloses an electrically conductive resin composition comprising a resin, a metallic powder, a diphosphonic acid derivative and an alcohol.

U.S. Patent No. 4,874,548 discloses an electrically conductive adhesive composition comprising an epoxy resin and conductive fibers.

Finally, United States Patent No. 5,376,403 concerns electrically conductive adhesive compositions, and methods for the preparation and use thereof, in which a solder powder, a chemically protected cross-linking agent with fluxing properties and a reactive monomer or polymer are the principal components. Depending upon the intended end use, the compositions comprise various combinations of a relatively high melting powder; solder powder; the active cross-linking agent which also serves as a fluxing agent; a resin; and a reactive monomer or polymer. The compositions are useful as improved conductive adhesives, such as for attaching electrical components to electrical circuits: the compositions comprising metal powder with high melting metals are ideally suited for creating the conductive paths on printed circuits. The compositions for forming conductive paths may first be applied to a substrate in the desired pattern of an electrical circuit, and then heated to cure it. During heating, the action of the cross-linking agent and optional reactive monomer or polymer within the mixture fluxes

the metals, enabling sintering to occur between the metal powder and the solder powder.

Attempts to produce conductive inks as a source of conductive traces to replace conventionally produced conductive traces of printed circuit boards have not met with commercial success for several reasons:

The electrical conductivity of metal filled polymer inks (Polymer Thick Film inks) as exemplified in US Patents 4,740,252; 4,888,135; 4,732,702; 4,678,602; 4,564,563; 4,725,500; 4,786,437 and electrically conductive adhesive compositions 4,830,779 and 4,874,548 is inherently very low, typically about 1% or less of copper film. This creates excessive resistance, and heat, in most circuits, limiting the use of this technology to low performance "niche" applications. Additionally, these products are not solderable, limiting their use only to applications that do not require subsequent assembly operations.

The electrically conductive compositions taught in Japanese Patents 0133799 and 0160072, and Japanese Patent Application JP 57-113505 provide improved electrical conductivity and solderability when compared to polymer thick films, but suffer from severe disadvantages as well.

Thus, while the electrical conductivity is improved, but only marginally, the chemical cross-linking (curing) of the resin begins well in advance of solder melting temperatures, increasing viscosity of the flux (which hinders the flux's ability to carry away oxides) and decreasing the concentration of active fluxing sites, which have been neutralised by reaction with resin. This results in electrical conductivity being improved only by a factor of 2 or less in relation to polymer thick film compositions.

These compositions are also based on relatively large metal particles which preclude their use in

printing fine line circuits. As virtually all circuit boards produced today have traces of 250 microns or less, these products will have a very limited utility. Since the surface area of metal particles increases exponentially as particle size is reduced, the inks made from fine ($\leq 10\mu$) particles have substantially more surface area, and consequently, substantially more metal oxides that need to be removed to facilitate metallic union, or sintering of the composition. As metallic powders become finer (smaller particles) more aggressive fluxing agents are needed to remove these oxides. The known compositions, therefore, require the addition of very strong fluxing materials and activators to allow the use of fine particles, and fine line printed circuits. These aggressive fluxing materials, and their decomposition products remain in the circuit trace, and can extensively damage the circuit by corrosion, of the metals and degradation of the polymer, and be a source of ionic contamination which will prematurely fail the circuit and electronic assembly.

These strong fluxing agents are also very reactive with the adhesive resins used in these inks, creating a stability problem for the ink composition. These products must thus be used very soon after they are mixed.

The electrically conductive composition described in US Patent 5,376,403 provided a marked improvement over earlier technology by improving electrical conductivity to 10% of that of copper, an order of magnitude improvement over PTF, and by providing a solderable composition that could be printed to produce fine line circuitry, but this product is not without major disadvantages. Thus, printed circuits produced with this material must be processed in an inert environment, preferably a vapour phase soldering

machine wherein the heating takes place in the vapour of a high temperature fluorinated fluid. This equipment is expensive, expensive to operate, and scarcely used in the printed circuit industry, limiting the utility of the composition. Moreover, the ink described is based on extensive use of brominated aromatic materials, which at the present time are subject to extensive inquiry into their effects on human health. A proposal has been made to ban their use in the European Polymers Industry.

Additionally, the use of alcohols to esterify the fluxing agent (and chemically protect it) is reversible, and the alcohol is regenerated as a substantial part ($\cong$ 50%) of the adhesive, weakening the bond strength and making the circuit liable to chemical attack.

The processing conditions described for the composition of USP 5,376,403 require an involved thermal profile which includes curing at 215°C and postcure at 150°C. These conditions promote the formation of intermetallic compositions know to degrade the performance of electrical conductors and interconnects by both increasing the resistance to current flow, and embrittling the trace. This problem is exacerbated by additional thermal processing, as is required to produce electronic assemblies.

Accordingly, it is an object of the present invention to provide improvements in the PCB production technology and, in particular, conductive ink compositions and precursors thereof which enable printed circuits to be produced quickly on a low-cost basis appropriate for both short and long production runs.

It is also an object of the present invention to provide improvements in the production of printed circuits with the aim generally of producing fully

additive multilayer interconnection.

In one aspect, this invention provides a composition of matter comprising the following components:

(a) a metal powder,

(b) a solder powder,

(c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being crosslinkable under the action of a chemical cross-linking agent,

(d) a chemical cross-linking agent for said polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis,

which metal powder and/or solder powder generates and/or has adhered thereto a catalyst

(e) for the cross-linking agent which is liberated on application of heat.

Component (a) is typically a metal powder of high melting point and high electrical conductivity. Component (b), by being a solder powder, is a low melting point constituent. Component (c) is preferably an epoxy resin, in particular a B stage epoxy resin. Component (d) is typically a polyacid to be described in detail hereinafter. Finally, component (e) may be an azole, such as benzotriazole, applied to powder (a) in particular as a stability enhancer.

This invention provides, in a second aspect, a composition on, or for application to, a dielectric substrate in a predetermined pattern comprising, in admixture

(i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low melting point constituent; and

(ii) a polyacid effective as a fluxing agent for the metallic powder component and as a cross-

linking agent for an epoxy resin at a first temperature and at a higher second temperature, respectively, the polyacid being in contact with such epoxy resin.

Compositions embodying this invention will be described hereinafter in detail and in their uses in terms of those according to the second aspect of the invention. However, it should be noted that compositions according to the first aspect of the invention have, through their embodying the same inventive principle, like uses.

The epoxy resin is generally an additional component of the composition when it is to be a conductive ink composition for use in the production of a printed circuit board. Alternatively, in producing a printed circuit board, an epoxy resin may be applied to a dielectric substrate by, for example, curtain coating or by patterning as a glue line and caused to interact with the metallic powder/polyacid combination of the composition subsequently applied to the dielectric surface.

The composition described herein can be processed in readily available air environment furnaces, contains no environmental or health damaging materials, and requires no post curing (intermetallic producing) processing.

In a third aspect, this invention provides a method of making an electrically conductive circuit on a dielectric surface comprising patterning a substrate with the admixture of metallic powder component and polyacid as aforesaid according to the second aspect of the invention, with either the epoxy resin being pre-coated on the substrate or the epoxy resin being incorporated in the patterned composition, and heating the admixture thus patterned to a temperature above the melting point of the low melting point constituent but below the melting point of the high melting point

constituent, being a temperature at which the polyacid is catalyzed by oxides liberated from the metallic powder, to achieve substantially complete crosslinking of the epoxy resin. When, as will be described hereinafter, the metallic powder is treated with an azole such as benzotriazole, such temperature will also be one at which the azole is liberated to take part in catalysis of cross-linking of the epoxy resin.

In a fourth aspect, this invention provides an electrically conductive circuit which comprises a metal film patterned upon a dielectric substrate and adhesively adhered thereto by a cured and cross linked epoxy resin, the metal film resulting from the patterning on the substrate of a composition comprising in admixture, (i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low melting point constituent and (ii) a polyacid effective as a fluxing agent for the metallic powder component and a cross-linking agent for an epoxy resin, an epoxy resin having been coated or patterned onto the dielectric substrate prior to patterning of said film. Upon heating to a temperature sufficient to melt the solder powder, the polyacid will flux the metallic powders, absorbing the liberated catalysts, and contact and mix with the pre-catalysed epoxy resin at the substrate / metallisation interface, incorporating and cross-linking said epoxy resin to provide a strongly adhered patterned metallisation upon the substrate surface. Preferably the epoxy resin is either one which is as a B stage resin or is a resin which can be B staged after application.

When practising the invention in accordance with its second, third and fourth aspects, reliance is placed on the co-use of the three components, components (i) and (ii) identified above and an epoxy resin. In this context, hereinafter, the term "ink"

will be used to denote printable compositions comprising components (i) and (ii) as aforesaid and which usually, but not always, will contain epoxy resin. A sophisticated relationship has been found to exist between these components in that the polyacid (ii) serves as a fluxing agent for the metallic powder component (i) so as to produce a metal oxide in sufficient amount so that, at elevated temperatures, it serves to catalyse a reaction between the epoxy resin and the polyacid (ii) then acting as curing agent. Although a simple acid could serve as a fluxing agent, a polyacid is necessary in the conductive ink composition in order to achieve cross-linking at two or more bonds of the epoxy resin.

Starting with the simplest component, the epoxy resin is preferably one which is liquid at ambient temperature and serves as an adhesive. The preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F.

The polyacid is preferably a polycarboxyl compound which serves as a fluxing agent for the metallic powders which produce metal oxide which is in turn a catalyst for reaction between the epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polycarboxyl compound may be a carboxylated polymer, a polycarboxylic acid or a polymer fatty acid, such as a dimerised or trimerised fatty acid. An organic trimer fatty acid having a functionality greater than 1 provides more than one reaction site with the epoxy resin serving to create a macromolecule that provides required adhesion. The aforementioned preferred carboxyl-containing polymers also provide multiple reaction sites.

The polyacid serves as a fluxing agent for the metallic powder component, removing metal oxide from the metallic powder component. This removal of the metal oxide permits the metal particles to coalesce and

provide a continuous metal conductor. Furthermore, the removed metal oxide is produced in sufficient quantity that, in the presence of applied heat, it catalyses a reaction between the epoxy resin and the carboxyl groups on the polyacid.

Another beneficial property of the carboxylated polymer/epoxy composition is the stability of the composition with respect to reaction and curing during storage under ambient conditions. This composition is capable of extended shelf life - greater than six months at ambient temperatures.

The carboxyl groups on the polymer are non reactive at ambient temperatures. The composition will only become reactive and cross link when in the presence of heat and catalyst. Catalysts for this reaction are metal oxides, metal salts, and imidazole materials. These catalysts are generated by heating the metal powders, which oxidise to produce oxides, the oxides possibly reacting with resin and/or solvent to produce salts. Alternatively, the catalysts may be made available with the thermal release of chelating agent (an imidazole) which may have been used to protect and deactivate the copper metal. The catalysts liberated are typically: lead oxide, stannous oxide, organic tin and copper salts, and benzotriazole.

The polyacid, particularly when a polycarboxylic acid, is preferably thermally stable at 215°C and has an acid number greater than 200 and a viscosity of less than 10 centipoise at 200°C. Preferably such polymer is a carboxyl containing polymer, in particular a styrene acrylic acid copolymer. The conductive ink composition preferably contains from 5 to 25% in total of epoxy resin and polyacid and from 95 to 75% weight of the metallic powder component. More especially, one part by weight of the mixture of polyacid and epoxy resin as used is mixed with approximately 9 parts by weight of metal powder component.

Insofar as the metal powder component is concerned, the relatively low melting point constituent includes a first metal and a second metal, with the first metal having an affinity for the high melting point constituent, an oxide of the second metal being a catalyst for the curing of the epoxy resin and the first and second metals being melted together to form a metal film in which is embedded particles of the high melting point constituent while the first and second molten metals form a matrix regions between the particles of the high melting point constituent, which matrix is rich in the second metal of the relatively low melting point constituent. In such a case in particular, especially when the epoxy resin is a constituent of the ink composition, the epoxy resin is preferably liquid at ambient temperature.

The preferred metal powder component will be a mixture of three metals. One metal is the high melting point constituent of high electrical conductivity and is typically selected from copper, gold, silver, zinc, aluminium, platinum, palladium, beryllium, rhodium, nickel, cobalt, iron, molybdenum, tungsten and/or a high melting point alloy of two or more of these metals. Such metal is preferably copper powder in the particle size range from 5 to 25 μm, more preferably normally 10 μm copper.

The relatively low melting point component then provides the other two metals. One of these metals is typically tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony, selenium and/or an alloy of two or more such metals. The preferred such metal is tin although, when a third metal is not present, it can be lead. When a third metal is present, this is preferably lead and then the two metals constituting the relatively low melting point component are preferably tin/lead (Sn-Pb), preferably as eutectic alloy (Sn 63). The particle

size of this lower melting point metal component is preferably also in the range of from 5 to 25 μm, being nominally 10 μm powder.

Additional components not hitherto specified may be present in the conductive ink compositions of this invention. Thus, improved performance is achieved when the copper powder which is preferably used as the high melting metal powder is cleaned and coated with a stability enhancer which is an organic chelation agent, preferably an azole such as benzotriazole whose decomposition products are also catalysts for the reaction between the epoxy resin adhesive and the polyacid and serve to bring about high density cross-linking without the need for any post-curing.

One further additional compound which may be present in the conductive ink composition is a reaction accelerator, preferably benzotriazole. Such azole compounds may be used to chelate metal, in particular copper, and are then released into the polymer matrix at the activation temperature, to serve as a catalyst to crosslink the epoxy/polyacid composition rapidly, providing a "snap cure" of the adhesive system present in a continual process. No post cure or further treatment is necessary.

In considering the use of the conductive ink composition embodying this invention, the following diverse chemical principals should be borne in mind:

(i) the low melting point metal component is preferably a tin/lead alloy which is oxidizable and has a lower melting temperature than the preferred high melting point metal, copper;

(ii) tin, as preferred low melting point metal, has, in its molten state, a particularly good affinity for copper;

(iii) tin and lead form, when melted together, a metal film;

(iv) the polyacid, preferably styrene acrylic acid copolymer, will flux both copper and tin/lead alloy;

(v) lead oxide and the decomposition products from benzotriazole are catalysts for the reaction between the epoxy resin adhesive and the polyacid; and

(vi) finally, and this is important in considering the stability of the conductive ink, copper powder catalyses the reaction between the epoxy resin and the polyacid. This needs to be eliminated or at least slowed down at ambient temperature.

In the production of printed circuit boards, the conductive ink is patterned on a dielectric substrate, which is normally pre-patterned with the epoxy resin when the epoxy resin is not present in the ink, patterning being effected, in general, by a screen printing process. The substrate, with ink applied, is then heated in an oven, preferably in a vapour phase oven that transfers heat quickly, to a temperature that is (1) above the lower melting temperature of the relatively low melting metal component but (2) less than the relatively higher melting temperature of the first metal, the respective metals being preferably tin/lead and copper. Unless otherwise indicated, these two metal components will be presented hereinafter as representative low and high melting point constituents as aforesaid. With these representative components, in particular, heating may be at 215°C for five minutes.

The high melting metal component (i.e. copper) and

the metal alloy powder (tin/lead) are both strongly fluxed by the polyacid which permits the molten tin to wet the surface of the copper. The chelate compound releases material from the surface of the Cu powder providing clean solderable copper surfaces. The tin/lead matrix becomes, in regions between the particles of the copper, rich in lead. A molten metal film coalesces, expelling both the epoxy resin and the polyacid to the surfaces of the film. Epoxy resin present in contact with the surfaces of the metal film is catalyzed by the metal oxide salts and possibly benzotriazole now present at the surface of the metal matrix and becomes rapidly cured and cross-linked. In the meanwhile, all of the acid groups will have reacted with the epoxide groups so as to neutralize the polyacid groups. A highly-electrically-conductive metal film strongly adhering to the dielectric substrate by a non-corrosive cured epoxy composition is then produced.

Thus, two conflicting objectives are satisfied, namely (1) a strong fluxing action which requires both a highly active reducing agent and a highly flowable low viscosity matrix, and (2) a reaction involving the polymer resin which is effective both to neutralise and immobilize the system while achieving adhesion to the substrate. Both of these are met.

The achievement of these objectives is met specifically by the conductive ink composition showing synergism when used in the manufacture of printed circuits. Thus (1) the polyacid of the conductive ink serves as a very effective chemical and mechanical flux for (2) the metallic content of the conductive film, permitting coalescesing of the high melting point metal component powdered particles within a metal film as a continuous conducting body having excellent electrical and mechanical properties. During curing of the epoxy resin, an oxide is present on the surface of the

metallic film and serves to catalyse curing and cross-linking of this resin-adhesive material and neutralizing of its acidity. Thus, one component promotes a change in the other component and vice versa. The net result of this synergism between resin-adhesive and the metallic components of the conductive ink composition is to produce a high quality metal film that may be strongly adhered to a dielectric substrate by a non-corrosive cured epoxy adhesive.

There is no wastage of materials in the production of printed circuits insofar as the conductive ink is concerned. Moreover, there is no emission of environmentally-harmful liquids or gases. The conductive ink itself is safe, non-toxic and stable on storage. The mechanical and electrical properties of the electrical circuit traces produced with the conductive ink match in quality those of normal (copper) printed circuit traces, typically exhibiting resistivity of less than 25 milliohms per square (at a thickness of 25μm), more preferably less than 10 milliohms per square (at a thickness of 25μm). Only small quantities of the conductive ink are required. In itself, the conductive ink is economical both for manufacture and use.

In accordance with the aforementioned fourth aspect of the invention, the stability and shelf life, or pot life, of conductive inks embodying this invention is greatly extended, typically by more than one order of magnitude, by taking certain steps in their preparation.

Firstly, when the high melting metal powder of the conductive ink is a copper powder, it is chelated with a very thin coating of a copper deactivator such as benzotriazole applied to the individual particles of the powder. This coating retards oxide or salt formation. The same chelation also serves desirably to prevent the catalytic effect of the high melting metal,

especially copper, in promoting prematurely the cross-linking of the resin. Upon release from the copper at activation temperature, the benzotriazole acts as a powerful catalyst for the curing reaction.

Secondly, an anti-oxidant copper deactivator, preferably oxalyl bis benzylidene hydrazine, is added to the resin to retard further the cross-linking reaction to which the resin is susceptible. The preferred oxalyl bis benzylidene hydrazine exhibits an inhibitory effect in a copper-containing epoxy resin reacted with a carboxylic resin by exhibiting a greater affinity for the unavoidably occurring copper salts than does the resin. Shelf life of copper-containing resin conductive ink, in particular, is typically increased by the aforementioned more than one order of magnitude when the inhibitor is present in the resin in a preferred concentration in the range of 0.25% to 5%, more preferably 1%, by weight.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made to the accompanying drawings to be referred to in the following description and the working examples, in particular. In the drawings:

Figure 1 is a diagrammatic representation of a cross-section through an epoxy resin-containing conductive ink embodying this invention when applied to a substrate but prior to heating thereof to cause flow of the relatively low melting metal constituent;

Figure 2 is a like view to that of Figure 1 but showing the condition of the ink after flow has occurred;

Figure 3 shows in greater detail a typical portion of the applied ink after such flow has taken

place, showing the constitution of different zones within the ink composition;

Figure 4 is a photomicrograph at 150x magnification of a printed /sintered ink embodying the invention over bare FR4 substrate.

Figure 5 is a photomicrograph at 300x magnification of a printed /sintered ink embodying the invention over a gold/nickel pad.

Conventional printed circuits are made by subtractive procedures in which circuit boards are laminated with one or more conductive layers which are etched to remove some portions of the conductive layer, leaving other portions according to a pre-determined circuit design. The technique involves relatively complex photographic procedures requiring large capital investments for etching and plating equipment and related apparatus, such as cameras. In general, the time required to design and produce a printed circuit by such conventional techniques is quite long and requires the use of skilled technicians. As a result, relatively few companies are capable of producing printed circuits using conventional techniques. Moreover because of the time and expense involved in preparing a printed circuit, standard procedures are not generally appropriate for short production runs, notwithstanding the desirability of the aimed printed circuit. The method of this invention is of assistance in enabling such reservations to be set aside, particularly because it enables screen printed technologies to be adopted.

When producing a conductive ink composition embodying this invention, the resin-adhesive component, when a component of the composition, is first mixed with the polyacid component. This mixture, or the

polyacid alone, as the case may be, and the optional exothermic compound, if used, is mixed with the constituents of the metallic powder component. The relatively low melting constituent thereof is susceptible to oxidation and is preferably an alloy of tin and lead in which it is the lead which is particularly subject to oxidation. Tin in such an alloy has an affinity for the high melting metal constituent. The oxide as aforesaid is a catalyst for the curing of the epoxy resin adhesive. The relatively low melting constituent of the metallic powder component is to form a metal film on melting.

Hereinafter, again, the invention will be described primarily with respect to the use of copper as high melting metal and a tin/lead alloy, in particular Sn 63, as relatively low melting constituent and the inclusion of epoxy resin in the ink. As already noted, the preferred tin/lead alloy is preferably of a particle size of 25 μm or less and is preferably of a particle size less than 10 μm. The particles of this and other low melting constituents are preferably first cleaned using, for example, a technique to be described in the examples which follow. Such cleaning is preferably to be applied to the high melting metal constituent. The acidic epoxy adhesive component, i.e. mixture of polyacid and epoxy compound, (and any optional exothermic compound) of the conductive ink preferably constitutes from 5 ~ 25% by weight thereof and the metallic powder component preferably constitutes from 95% ~ 75% by weight thereof. The acidic epoxy adhesive component is particularly preferably present in an amount of 10% by weight of the conductive ink and the metal powder component is then preferably present in an amount of approximately 90% by weight.

Insofar as the metallic powder constituent is concerned, preferably the higher melting point metal

(normally copper) constitutes up to 90% by weight, more preferably 67% by weight of the component. The preferred metal alloy component (normally tin/lead) preferably amounts to from <100% to 10% by weight, more preferably amounting to 33%.

The stability of conductive inks embodying this invention during storage and use may be maintained for relatively long periods, and for generally longer times than heretofore. This improved stability helps minimise quality problems in the production of printed circuits using the inks. Improved stability may be achieved in one or both of two ways.

Firstly, the high melting metal component, normally copper powder, is chelated with an organic coating, preferably a benzotriazole in an extremely thin coating over the individual particles. This coating neither affects the electrical conductivity nor degrades the solder wetting characteristics of the powder. Such chelating coatings are well known in the art as a means of preventing oxide formation on copper materials and are commonly used to maintain the solderability of copper lands on printed circuit boards. Such coatings have also been employed in copper powder paints to reduce oxidation and to maintain electrical conductivity when conductivity is dependent upon physical contact between individual metal particles in the powder since oxide formation reduces conductivity.

However, in the practice of the present invention, the chelation of the copper also serves to prevent the catalytic effect of the copper in promoting the cross-linking of the resin.

Moreover, a novel anti-oxidant copper deactivator may be added to the resin to enhance such inhibition of catalytic effects of the copper on the cross-linking of the resin. A preferred such deactivator is oxalyl bis benzylidene hydrazine. Copper deactivators, such as

this compound, have previously found commercial application in preventing embrittlement of polyethylene hook-up wire when it comes into contact with copper metal. This embrittlement was caused by an oxidated cross-linking and degrading of the polymer by copper salts. However, no previous use of a copper deactivator in combination with epoxy resin has hitherto been described.

The preferred oxalyl bis benzylidene hydrazine material exhibits an inhibitory effect in a copper-containing epoxy resin reacted with a carboxylic resin. The inhibitor is effective by its exhibiting a greater affinity for the copper salts than the resin. Shelf life of copper-containing resin conductive ink is then typically increased by more than one order of magnitude when the inhibitor is present in the resin in a preferred concentration in the range of 0.25% to 5%, more preferably 1% by weight.

A printed circuit board may be produced using the conductive ink of the invention by patterning on a dielectric substrate, normally by a screen-printing process. The applied ink will have the appearance shown in cross-section in Figure 1. The substrate with the conductive ink composition patterned thereon is then heated to a temperature intermediate the melting points of the two constituents of the metallic powder component. The acid component then serves as a fluxing agent to the oxidizable higher melting metal powder as well as for the relatively low melting metal constituent. It removes oxide from the surface of particles of the metals present, permitting the relatively lower melting point metal to wet the surface of the first metal to which it has a considerable affinity when the respective metals are tin and copper. The ink will now be as shown in Figure 2. Figure 3 shows the condition of the ink in greater detail with reference to the use of Cu and Sn63/Pb37 for the two

metal powders.

The present invention has been described generally herein with respect to the additive provision of circuit patterns by printing of the inventive ink on a dielectric substrate with epoxy resin being present either in the ink or as a coating applied to the substrate and serving to act as an adhesive for the patterned circuit to the substrate. This principle may also be applied to the production of multilayer printed wiring boards in which a plurality of layers is produced in accordance with the method of the invention and laminated together with interposition of dielectric layers between conductive layers. The metal traces produced must here be resistant to melting when further heating takes place to achieve bonding together of the layers. Particularly with such multi-layer structures, there is a need to provide interconnections between the circuits of individual layers. Vias for this purpose are typically formed in a PCB by for example drilling, punching, laser drilling or etching in a circuit after an adhesive has been applied to the dielectric side of the circuit, and provide electrical connection between circuits at different levels in an overall structure or serve merely to provide a connection between applied components and a printed circuit. There is a need for there to be a good filling degree of conductive material in the via and good adhesion of such material to the wall of the via. Via filling compositions are frequently of a pasty nature and enter the vias by application of a via-filling composition to the printed circuit board and application of a doctor blade to ensure entry into the via. Compositions embodying this invention which contain an epoxy resin meet the aforesaid requirements of via formation eminently owing to the quality of adhesion attainable through the presence of metal oxide produced on reaction between the polyacid fluxing agent and the metal powder, which

adhesion may be enhanced as a result of other cross-linking enhancing factors described hereinabove.

Thus, this invention also provides a multilayer wiring board in which vias connecting electrically conductive circuits contain a metal filling resulting from filling the vias with a composition according to the first aspect of the invention having the epoxy resin contained therein and heating to a temperature between said first and second temperatures to cure and crosslink the epoxy resin and cause the via filling to adhere to the via walls.

Although reference has been made hitherto to the printing of compositions embodying this invention on a dielectric substrate and the achieving of a good adhesion thereto, adhesion may be enhanced by provision of channel formations patterned on the substrate.

Thus in one procedure, the epoxy resin is pre-coated on the dielectric substrate, a photoimageable layer is applied to the adhesive layer, the photoimageable layer is subjected to a photoimaging and developing process to form a channel pattern in the photoimageable layer corresponding to the circuit, said admixture is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve substantially complete crosslinking of the epoxy resin.

In an alternative procedure, a photoimageable layer is applied to the dielectric substrate and subsequently subjected to a photoimaging and developing process to form a channel pattern. Said admixture, additionally containing the epoxy resin, is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve substantially complete crosslinking of the epoxy resin.

This principle of channel patterning may be applied to each of the plurality of layers involved when producing a multilayer wiring board. Further

particulars of the channel patterning technique are to be found in WO-96/22670.

The compositions of this invention find use in a number of areas of electronics and PCB/wiring board technology to be described hereinafter. Specific circuit features to be indicated hereinafter will be formed of a composition embodying this invention having the epoxy resin incorporated therein and will have been heated in-situ to a temperature sufficient to melt the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

For example, the compositions of this invention may be used in this way as an alternative to soldered wires for the repair and/or modification of conventional etched copper printed wiring boards.

Although described primarily as having use in the production of laminar circuits as in printed circuit boards, because compositions embodying this invention have practical use as polymer thick films, the composition may then have a structural function. For example the compositions may be employed in the formation of thermal transfer pillars in the construction of semi-conductor packages, multichip modules, etc. The compositions may also be used to form conductive terminations for printed potentiometer tracks giving extremely low contact resistance through the wiper of the potentiometer assembly by being extremely resistant to wear.

Particularly insofar as the compositions of the invention may provide a conductive adhesive, they may then function as a replacement for solder in the joining of electronic components to conductive "lands" on substrates. The compositions may also be utilised to operate simultaneously as conductive tracers and as

conductive adhesive on a substrate, thus requiring no "lands" for the electrical connection of electronic components. In this case, cross-linking should not be completed before applying the electronic components.

A further area of use of compositions involving this invention is as a shielding layer on printed wiring boards for the suppression of electromagnetic interference (EMI)/radio-frequency interference (rfi). Such uses have particularly relevance to the production of cellular telephones.

The invention may be better understood by reference to the following examples which are intended for purposes of illustration and are not to be construed as in any way limiting the scope of the present invention, which is defined in the claims appended hereto. The following materials were used when carrying out the Examples:

Materials	Source
SnPb solder alloy (63:37), 10-25μm particle size	Multicore Solders Ltd.
Copper powder, <20 μm particle size	ACuPowder International
Entek Plus 106A, benzotriazole passivation system for copper	Enthone-OMI
"SF-50" silver flake, ≤ 0.4 μm particle size, optionally added to the ink formulation to modify rheology	Degussa
Joncryl 682, styrene-acrylic copolymer which is the cross-linking agent and primary fluxing agent	SC Johnson
Epikote 862, (uncrosslinked) epoxy resin	Shell
OABH inhibitor, anti-oxidant	

copper deactivating agent (oxalyl bis benzylidene hydrazine)	Eastman
Modaflo, a rheology modifier optionally added to formulations to enhance flow of epoxy resin prior to cross-linking	Monsanto
Silquest A-187 Silane, a coupling agent optionally added to formulations to promote better adhesion	OSI Specialties
3, 3-Thiodipropionic acid, an optional secondary activator	
Butyl carbitol, solvent	Aldrich

Inks were prepared in several stages in the Examples:

* metal powder preparation
* styrene-acrylic copolymer solution preparation
* activator system preparation
* ink base preparation
* fully formulated ink preparation
* final adjustment of ink.

Example 1

Preparation of Metal Powders

The copper powder was immersed in 5% v/v sulphuric acid at 80°C until it exhibited a bright salmon colouration. It was then collected by filtration and thoroughly rinsed with deionised water and dried. Cleaned copper powder was treated with Entek Plus 106A. The solder powder was cleaned in a 10% w/w aqueous solution of ammonium bifluoride before being collected, rinsed and dried.

Preparation of Styrene-Acrylic Copolymer Solution

50 g of butyl carbitol were added to 100 g of Joncryl

682. This mixture was stirred over a hotplate at 120°C until a clear pale yellow solution was obtained. This was stored in an air tight bottle at room temperature pending use in the next stage.

Preparation of Ink Base

75 g of the styrene-acrylic copolymer solution were placed in a 400 cm^3 beaker. 50 g of Epikote 862 were added, along with 0.5 g of Modaflo, 0.25 g of Silquest A-187 and 1.0 g OABH. This mixture was homogenised with a spatula and stored in a sealed plastic jar pending ink preparation.

Preparation of Activator System

The styrene-acrylic copolymer solution did not confer sufficient fluxing activity. Therefore, a secondary activator was incorporated. This was prepared as follows:

5 g of 3,3-thiodipropionic acid were added to 10 g of butyl carbitol. The mixture was warmed to form a colourless solution (although there was precipitation on cooling).

Preparation of Fully Formulated Ink

10 g of ink base was weighed into a 125 cm^3 beaker. 60 g of cleaned/passivated copper powder, and 30 g of cleaned solder powder were added. These ingredients were mixed with a spatula for about ten minutes.

Final Adjustment

The rheology of the ink was adjusted to facilitate printing by the addition of extra butyl carbitol and SF-50 silver flake.

Sintering was investigated by floating a thin film of ink smeared across a microscope slide on a solder bath at 235°C. Sintering (ie solder-copper wetting) is indicated by a change in colour from brown to grey. This only occurred when a small amount of the prepared activation system was added; this was first homogenised in view of the precipitation which occurred.

Assessment of Fully Formulated Ink

The composition of the fully formulated ink is given

in Table 1.

Table 1: Composition Of The Fully Formulated Ink

All data are in wt%.

Ink Component	Amount
Ink base	9.70
Activator system	0.77
Butyl carbitol	1.90
Copper powder	58.10
Solder powder	29.00
SF50 silver flake	0.48
Activator System	
3, 3-Thiodipropionic acid	33.33
Butyl carbitol	66.67
Ink Base	
Styrene-acrylic copolymer solution	59.15
Epikote 862	39.45
Modaflo	0.40
Silquest A-187	0.2
OABH	0.80
Styrene-acrylic copolymer solution	
Joncryl 682	66.67
Butyl carbitol	33.33

The ink was assessed in several ways:

* fineness of grind
* viscosity profile
* printing characteristics
* electrical properties of sintered ink

The fineness of grind measurement indicated some agglomerated particles above 50μm. These broke down during testing.

Ink viscosity at 25°C was measured using a Brookfield HBT viscometer fitted with a an SC4-14/16R spindle. The results are tabulated in Table 2:

Table 2

Speed (rpm)	Fineline Ink (cps)
1	250,000
2.5	200,000
5	180,000
10	150,000
20	130,000
50	90,500
100	69,000
50	80,000
20	100,000
10	120,000
5	140,000
2.5	160,000
1	200,000

To test printing characteristics, ink was printed with a DEK245 printer onto FR4 substrate which had been degreased with acetone and stored for two days in an air-circulating oven at 60°C to remove trapped moisture. Three screens were used. The results are shown in Table 3.

Table 3

Screen	1	2	3
Mesh/inch	180	180	230
Mesh type	Stainless steel	Stainless steel	Stainless steel
Mesh orientation/°	90	45	90
Emulsion thickness	15 (97-112)	12 (95-107)	12 (77-89)/μm
Printing parameters			
Printer speed /mm s^{-1}	44	44	44
Squeegee type	Diamond, 45°	Diamond, 45°	Diamond, 45°
Squeegee pressure /Kg	5.5-5.6	4.6-4.7	6.1-6.2
Substrate type	Blank FR4	Cu / FR4 Au/Ni/FR4	Blank FR4

The ink rolled well on all screens with no skidding. Print definition was good, and there was no bleeding with two of the three screens. Four thou lines with the third screen were ill defined, probably due to the FOG (four thou = 100μm, i.e. twice the size of some agglomerated particles); in addition, there was very slight bleeding.

Printed PCBs were dried for 5 minutes in an air-circulating oven at 120°C to remove solvent. The thickness of the dried ink was then measured using a Taylor-Hobson Talysurf 10 surface texture measuring instrument:

Screen	1	2	3
Thickness/μm	40-42	56-58	32-35

Finally, printed PCBs were reflowed in a vapour phase reflow oven at 215°C for 4 minutes with a short (1 minute) dwell time at 50°C before and after.

Successful flow of the solder to achieve a coalesced metal film was achieved in all cases. Further measurements using the Taylor-Hobson Talysurf 10 surface texture measuring instrument indicated no modification in print thickness.

The sintered ink was assessed for electrical resistivity using a four-probe method, with the print thickness normalised to 25 μm:

Screen	3	1
Resistivity /mOhm/square	10.5	15

Solderability was investigated by applying low solids liquid flux to the sintered ink, followed by brief exposure to 60/40 Sn/Pb solder at 235°C. The sintered ink was successfully soldered.

The character of the conductive layer was

investigated by microscopic examination of a sectioned specimen at 300x magnification (Figure 4). This suggested a good degree of metal fusion. Ability to wet metallic surfaces during sintering was assessed using the patterns printed with Screen 2 (Figure 5). Both the copper and gold surfaces became coated with solder. This is important in considering the present invention as a conductive "adhesive" for joining electronic components to printed circuit boards.

Finally, there was a brief shelf life study. A one gram sample was placed in a air circulating oven at 60°C for 24 hours. There was no sign of modified physical properties or premature curing.

Example 2

A specimen of the ink from Example 1 was successfully sintered under air using a Sikama hot belt reflow station. The resistivity was the same as that given by an identical sample sintered in parallel using a vapour phase reflow oven.

Examples 3-6

Following the success of the preceding examples, further batches of ink were prepared in the same manner as in Example 1 and used to investigate the role of the various components and metal powder treatments. Typical data given in Table 4 underline the complexity of the formulation process with both composition and treatment impacting upon stability, sintering capability and resistivity. The data presented are for illustrative purposes only.

Table 4: Modification of Ink Composition

All amounts are in grams.

Example	3	4	5	6
Ink base				
Styrene-acrylic copolymer solution*	29.58	29.58	29.58	29.58
Epikote 862	19.72	19.72	19.72	19.72
Modaflo	0.2	0.2	0.2	0.2
Silquest A-187	0.1	0.1	-	-
OABH	-	0.4	-	0.4
3,3-Thiodipropionic acid	0.13	0.13	0.13	0.13
Butyl carbitol	1.2	1.2	1.2	1.2
Ink base properties				
Viscosity at 20rpm/cP	8500	8900	11200	9400
Stability after 2 weeks	OK	OK	OK	OK
Stability after 8 weeks	Becoming thick	Slightly sticky	Slightly sticky	Slightly sticky
Ink				
Ink base	5.00	5.00	5.00	5.00
Copper powder	22.50	22.50	30.00[1]	30.00[2]
Solder powder	21.35	21.35[2]	14.23[2]	14.23
Extra butyl carbitol	1.50	-	1.50	-
Ink properties				
Stability after 1 week	Slight skin		Poor	PoorOK
Stability after 3 weeks	Early cure stage		-	--
Sintering capability	90%	None	70%	50%
Resistivity of sintered ink / mOhm/square/25 µm	18.8	3132	19.8	25.5

* Exactly the same as in the first example.

1 Copper cleaned and Entek Plus 106A coated (otherwise copper is cleaned but not passivated)

2 Cleaned solder alloy

A prerequisite for all chemicals used in the manufacture of electrical products is ionic cleanliness: this minimises the possibility of in-service reliability problems. Therefore, inks sintered during this stage of the product development process were also subjected to ionic contamination assessment using the Multicore CM11 Contaminometer. All exhibited low ionic contamination below 0.2 μg NaCl eq/cm^2, easily in line with the demands of industry standards such as MIL-P-28809A.

CLAIMS:-

1. A composition of matter comprising

(a) a metal powder,

(b) a solder powder,

(c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being crosslinkable under the action of a chemical cross-linking agent,

(d) a chemical cross-linking agent for said polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis,

which metal powder and/or solder powder generates and/or has adhered thereto a catalyst

(e) for the cross-linking agent which is liberated on application of heat.

2. A composition according to Claim 1, wherein said metal powder is selected from Au, Ag, Cu, Zn, Al, Pd, Pt, Rh, Fe, Ni, Co, Mo, W, Be, and alloys thereof.

3. A composition according to Claim 2 wherein said metal powder is copper.

4. A composition according to Claim 1, 2 or 3, wherein said solder powder is selected from Sn, Bi, Pb, Cd, Zn, Ga, In, Te, Hg, Sb, Se, Tl and alloys thereof.

5. A composition according to Claim 4 wherein said solder powder alloy is Sn63Pb37.

6. A composition according to any preceding claim wherein said latent chemical cross-linking agent is selected from carboxylated polymers, dimer fatty acids, and trimer fatty acids.

7. A composition according to Claim 6 wherein said

patent chemical cross-linking agent is a styrene-acrylic acid copolymer.

8. A composition according to any preceding claim wherein said catalyst is generated by oxidation of solder powder and liberated from the solder powder by the fluxing agent.

9. A composition according to Claim 8 wherein said catalyst is generated by oxidation of tin and/or lead powder and liberated from the powder by the fluxing agent.

10. A composition according to Claim 1 wherein said catalyst is generated by reaction of metal powder or solder powder with resins or solvent to produce organo-metal salts.

11. A composition according to Claim 10 wherein said catalyst is generated by reaction of tin with resin or solvent to produce tin salt.

12. A composition according to Claim 10 wherein said catalyst is generated by reaction of copper with resin or solvent to produce copper salts.

13. A composition according to any preceding claim, wherein said catalyst is an organic chelating agent adhered to the metal powder and liberated at solder melting temperature into the fluxing agent.

14. A composition according to Claim 13 wherein said catalyst is an azole chelating agent.

15. A composition according to claim 13 wherein said catalyst is benzotriazole

16. A composition according to any preceding claim further comprising an organic surface protectorant chelate coating the metal for stability enhancement.

17. A composition according to Claim 16 wherein said organic surface protectorant is benzotriazole.

18. A composition according to any preceding claim further comprising a copper salt deactivator as a stability enhancer.

19. A composition according to Claim 18 wherein said copper salt deactivator is oxalyl bis benzylidene hydrazine.

20. A composition on, or for application to, a dielectric substrate in a predetermined pattern comprising, in admixture:

(i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low melting point constituent; and (ii) a polyacid effective as a fluxing agent for the metallic powder component and as a cross-linking agent for an epoxy resin at a first temperature and at a higher second temperature, respectively, the polyacid being in contact with such epoxy resin.

21. A composition according to claim 20 which has the epoxy resin in admixture with the metallic powder constituent and the polyacid.

22. A composition according to claim 20, which has the epoxy resin pre-applied to the dielectric substrate.

23. A composition according to claim 22, wherein the epoxy resin is printed on the substrate in a

predetermined pattern.

24. A composition according to any one of claims 20 to 23, wherein the polyacid is thermally stable to 215°C and has an acid number greater than 200 and a viscosity less than 10 centipoise at 200°C.

25. A composition according to one of claims 20 to 24, wherein the polyacid is a polycarboxyl compound which serves as a fluxing agent for the metallic powder so as to produce a metal oxide which, in turn, is a catalyst for the reaction between the epoxy resin and carboxyl groups of the carboxyl-containing polymer at said second temperature.

26. A composition according to claim 25, wherein the polycarboxyl compound is selected from: carboxylated polymers, polycarboxylic acids and polymer fatty acids.

27. A composition according to claim 26, wherein the polymer fatty acid is a dimer or trimer fatty acid.

28. A composition according to claim 26, wherein the carboxylated polymer is a styrene-acrylic acid copolymer.

29. A composition according to any one of claims 20 to 28, wherein the metal powder component contains up to 0 to 80% by weight of the high melting point constituent of high electrical conductivity and from <100 to 20% by weight of the relatively low melting point component.

30. A composition according to any one of claims 20 to 29, wherein the high melting point constituent of the metallic powder component is a metal selected from Au, Ag, Cu, Zn, Al, Pd, Pt, Rh, Fe, Ni, Co, Mo, W, Be, and alloys thereof.

31. A composition according to any one of claims 20 to 30, wherein the low melting point constituent of the metallic powder component is selected from Sn, Bi, Pb, Cd, Zn, Ga, In, Te, Hg, Sb, Se, Tl and alloys thereof.

32. A composition according to any one of claims 20 to 31, wherein the relatively low melting point constituent includes a first metal and a second metal, with the first metal having an affinity for the high melting point constituent, an oxide of the second metal being a catalyst for the curing of the epoxy resin and the first and second metals being melted together to form a metal film in which is embedded particles of the high melting point constituent while the first and second molten metals form a matrix in regions between the particles of the high melting point constituent, which matrix is rich in the second metal of the relatively low melting point constituent.

33. A composition according to claim 32, wherein the relatively low melting point constituent is a tin/lead alloy.

34. A composition according to claim 33, wherein the high melting point constituent is copper.

35. A composition according to any one of claims 20 to 34, wherein the metallic powder component has particles of a size less than 25μm.

36. A composition according to any one of claims 20 to 33, wherein the epoxy resin consists essentially of an epoxy resin which is liquid at ambient temperature.

37. A composition according to any one of claims 20 to 36; which contains, in percent by weight, from 5 to 50% in total of epoxy resin and carboxyl-containing polymer

and 95 to 50% of the metallic powder component.

38. A composition according to any one of claims 20 to 37 wherein the high melting point constituent is a copper powder which has been cleaned and coated with a stability enhancing copper deactivator which is a chelation agent for the copper and a high temperature catalyst for the crosslinking of the epoxy resin.

39. A composition according to claim 38, wherein the chelation agent is an azole compound.

40. A composition according to claim 39, wherein the chelation agent is benzotriazole.

41. A composition according to any one of claims 20 to 40, wherein the high melting point constituent of the metallic powder component is copper powder and the composition additionally includes anti-oxidant copper deactivating agent.

42. A composition according to claim 41, wherein the anti-oxidant copper deactivating agent is oxalyl bis benzylidene hydrazine.

43. A method of making an electrically conductive circuit on a dielectric surface comprising patterning a dielectric substrate with the admixture of metallic powder component and polyacid as specified in claim 20 with either the epoxy resin of claim 20 being pre-coated on the substrate, or the epoxy resin being incorporated in the patterned composition, and heating the dielectric substrate thus patterned to a temperature above the melting point of the low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable but highly

active as a fluxing agent to achieve metallic sintering and catalyzed crosslinking of the epoxy resin.

44. The method of claim 43, wherein the epoxy resin is pre-coated on the dielectric surface by patterning and the composition is applied to the epoxy resin pattern by matching patterning.

45. A method as claimed in claim 44, wherein the epoxy resin is pre-coated on the dielectric substrate, a photoimageable layer is applied to the adhesive layer, the photoimageable layer is subjected to a photoimaging and developing process to form a channel pattern in the photoimageable layer corresponding to the circuit, said admixture is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve metallic sintering and substantial crosslinking of the epoxy resin.

46. A method as claimed in claim 43, wherein a photoimageable layer is applied to the dielectric substrate and subsequently subjected to a photoimaging and developing process to form a channel pattern, said admixture additionally containing the epoxy resin is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve metallic sintering and substantial crosslinking of the epoxy resin.

47. A method as claimed in 46 wherein the epoxy resin is coated into the channel of the dielectric substrate and "B" staged prior to the application of the admixture.

48. A method as claimed in claim 45, 46 or 47, wherein the track is formed with an undercut region in side walls thereof.

49. A method as claimed in 43 wherein the epoxy resin is applied to the entire dielectric substrate and "B" staged to produce a dry handleable substrate allowing for subsequent patterning of said admixture to said substrate.

50. An electrically conductive circuit which comprises a metal film patterned upon a dielectric substrate and adhesively adhered thereto by a cured and cross-linked epoxy resin, the metal film resulting from the provision, patterned on the substrate, of a composition according to any one of claims 1 to 42 followed by heating of the composition to a temperature sufficient to melt the solder powder or low melting constituent and coalesce the metallic film produced.

51. A method of making a multilayered electrically conductive circuit by first applying and curing an insulating dielectric layer on a single layer electrically conductive circuit produced according to the method claimed in any one of claims 43 to 49 the insulating dielectric layer having vias, and forming a second electrically conductive circuit on the cured dielectric layer by the method claimed in any one of claims 43 to 49 and repeating these steps to form a required plurality of alternating dielectric layers and electrically conductive circuit layers.

52. A method according to claim 51, wherein said vias are filled with a metal filling resulting from filling them with a composition according to any one of claims 20 to 42 having the epoxy resin contained therein and heating to a temperature sufficient to melt the relatively low melting constituent, coalesce the metals present, cure the epoxy resin and cause the via filling to adhere to the via walls.

53. A multilayer printed wiring board in which vias connecting electrically conductive circuits contain a metal filling resulting from filling the vias with a composition according to any one of claims 20 to 42 having the epoxy resin contained therein and heating to a temperature sufficient to melt the relatively low melting constituent solder powder, coalesce the metallic film, cure the epoxy resin and cause the via filling to adhere to the via walls.

54. A thermal transfer pillar in a semi-conductor package and/or a multichip module, which is formed of a composition as claimed in any one of claims 20 to 42 having the epoxy resin incorporated therein and which has been heated in-situ to a temperature sufficient to melt the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

55. An electrically conductive termination for a printed potentiometer track, which is formed of a composition as claimed in any one of claims 20 to 42 having epoxy resin incorporated therein and which has been heated in-situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

56. A conductive track joining leads on a printed circuit board, or other substrate usually for the purpose of repair or modification, the conductive track being formed of a composition as claimed in any one of claims 20 to 42 having the epoxy resin incorporated

therein and which has been heated in situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial complete crosslinking of the epoxy resin.

57. A shield layer on a multilayer printed wiring board for suppressing of electromagnetic interference or radio-frequency interference, which layer is formed of a composition as claimed in any one of claims 20 to 42 having epoxy resin incorporated therein and which has been heated in-situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

58. A method of joining electronic components to substrates whereby the composition as claimed in any one of claims 1 to 42 is used as an electrically conductive adhesive to adhere the electric components to a said substrate.

59. A method as described in Claim 58, where the substrate has been produced by a method as claimed in any of claims 43 to 49, 51 and 52 and the electronic components are placed into the said composition prior to the temperature being raised, the substrate is then heated to said temperature thus forming the electrically conducting circuit and joining the electronic components simultaneously to an electrically conductive circuit.